METHANOL FORMATION IN THE PYROLYSIS OF FORMALDEHYDE

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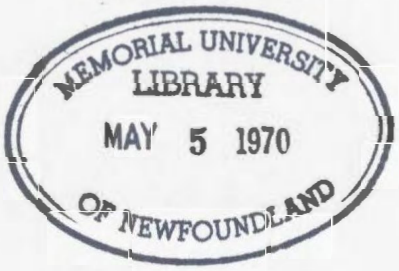
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METHANOL FORMATION IN THE PYROLYSIS OF FORMALDEHYDE

by

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A Thesis

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in partial fulfillment of the requirements
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to my mother and father

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ABSTRACT

The pyrolysis of formaldehyde has been studied at 420° C and 452° C in the pressure range 20-130 mm. The products are mostly carbon monoxide, methanol and hydrogen as previously reported. The ratio $(CH_3OH)/(H_2)$ is approximately four at 420° C and one at 452° C. When formaldehyde was completely pyrolyzed a good carbon balance was obtained, indicating that no condensation reaction occurred, at least at the end of the reaction. Reports of a condensation reaction have appeared in the literature.

Conditioning of the reactor by pumping over night with the oil diffusion pump had no effect upon the rate of methanol formation. The rate of hydrogen formation was sometimes erratic. As the reactor aged the rate of hydrogen formation decreased slightly but no effect on methanol formation could be detected.

The addition of foreign gas (CO_2) increased the rate of hydrogen formation, but had no effect upon the rate of methanol formation.

The reaction is approximately second order for methanol with a suggestion of temperature dependence of order. Hydrogen formation is also approximately second order but the results are erratic. For H_2 the observations are consistent with the results of previous work at ≃ 500° C and at ≃1500° C

and for CH_3OH they are consistent with some preliminary results which have been reported. Activation energies estimated for methanol formation and hydrogen formation were 31 and 39 kcal mol^{-1} respectively.

A radical chain mechanism for methanol formation is proposed which, when combined with a mechanism for hydrogen formation, can account for all of the observations in the present work: the reaction orders, the dependence of the rate of formation of H_2 on foreign gas pressure and the independence of the rate of formation of CH_3OH on foreign gas pressure, the sometimes erratic rate of H_2 formation and the reproducible rate of CH_3OH formation. The activation energy estimated from this mechanism is close to the experimental value for CH_3OH. The mechanism, however, cannot explain the large increase in the rate of hydrogen formation found by Klein in the unbaked vessel and by Ke in the unconditioned vessel. Heterogeneous reactions occurring in the unbaked or unconditioned vessels are therefore proposed.

INTRODUCTION

A number of investigations have been made of the pyrolysis of formaldehyde over the past thirty years.

Fletcher (1), by measuring the pressure changes between 510 and 607° C, found that the reaction occurred in two stages, a rapid stage followed by a slow stage. Near the end of the first stage the ratio $(CO)/(H_2)$ in one experiment was reported to be 1.37, while at the end of the second stage in two experiments it was 1.06 and 1.09. Packing the vessel decreased the initial rate of pressure change in the first stage as well as the pressure change at the end of the first stage. The total pressure increase in the unpacked vessel was approximately 90% and in the packed vessel approximately 70%. Also, the pressure increase in the first stage was smaller at high reactant pressure, but the pressure increase in the second stage was greater.

Fletcher proposed that in the first stage of pressure increase the reactions included

$$\text{I.} \quad CH_2O \rightarrow \tfrac{1}{2}CH_3OH + CO$$

$$\text{II.} \quad CH_2O \rightarrow CO + H_2,$$

therefore the ratio $(CO)/(H_2)$ is greater than one. He proposed that in the second stage CH_3OH decomposed to H_2 and CO, reaction III,

$$\text{III.} \quad CH_3OH \rightarrow 2H_2 + CO,$$

giving a $(CO)/(H_2)$ ratio of almost one at the end of the reaction.

The inhibition by packing of the initial rate of pressure rise possibly indicates inhibition of reaction II. However, packing decreases the pressure rise in the first stage and also in the second stage, showing that the smaller pressure rise is not simply due to the presence of more CH_3OH, but is (at least partly) due to a condensation reaction.

Fletcher, using the method of plotting the reciprocal half-time vs initial pressure, calculated that the reaction was second order; of course referring to reaction II.

Patat and Sachsse (2), by measuring the rate of conversion of para to ortho hydrogen during the pyrolysis of formaldehyde, estimated that the H atom concentration was only 10^{-4} of that calculated from a Rice-Herzfeld mechanism. They concluded that a chain reaction was not involved.

Steacie and Alexander (3), in their investigation of the use of deuterium labelled compounds as indicators for the presence of free radicals in organic decomposition reactions, also concluded that formaldehyde does not decompose by a free radical mechanism. They pyrolyzed mixtures of CD_3COCD_3 and CH_3OCH_3. The pyrolysis of CH_3OCH_3 was assumed to produce CH_2O which subsequently decomposed,

$$CH_3OCH_3 \rightarrow CH_4 + CH_2O$$

$$\text{II.} \qquad CH_2O \rightarrow CO + H_2$$

If hydrogen atoms were produced in reaction II, HD might be produced,

$$H + CD_3COCD_3 \rightarrow HD + CD_2COCD_3.$$

The hydrogen formed was mainly H_2.

However, Kodama and Takezaki (4) and Longfield and Walters (5), who studied the radical-sensitized decomposition of formaldehyde, and Klein, Scheer and Schoen (6), who studied the pyrolysis of formaldehyde, suggested that decomposition occurred thermally by a chain mechanism. Both Kodama and Longfield found that methyl radicals sensitize the decomposition to H_2 and CO, indirect evidence that reaction II occurring in pure CH_2O is a radical chain reaction. Klein found direct evidence of a radical chain reaction. He observed that thermal decomposition of a mixture of CH_2O and CD_2O (without exchange to CHDO) gives H_2, D_2 and HD in proportions consistent with a radical reaction. He also pyrolyzed mixtures of $CH_2O$and D_2. He interpreted the results as showing that although the hydrogen atom concentration is small, it exceeds that which would be expected from the thermal decomposition of hydrogen alone.

Klein suggested that a condensation reaction occurred as well. If it is assumed that the pyrolysis of formaldehyde gives only CO, H_2 and CH_3OH as products, P_{H_2} should be equal to ΔP. The result showed that P_{H_2} was always somewhat larger than ΔP, indicating a condensation reaction. The rate of formation

of H_2 was found to be independent of the surface to volume ratio, using fused silica reaction vessels differing in their S/V ratio by a factor of 9. The rate of decomposition leading to hydrogen formation, as reported by Klein, is affected by the treatment and history of the reaction vessel. In order for the reaction rate to be independent of the surface to volume ratio, both initiation and termination steps have to occur in the surface, or both not in the surface. From the proposal of wall termination in the photolysis of formaldehyde (7), Klein suggested that both initiation and termination occur at the wall.

While Fletcher's (1) analysis of non-condensable products showed that the reaction at temperatures above 510° C yields mainly hydrogen and carbon monoxide, and only a very small amount of methanol, Calvert and Steacie (7) reported that in the temperature range 150 to 350° C carbon monoxide and methyl alcohol, detected by mass spectrometric analysis, were found as the major products. Above 300° C a small but increasing quantity of hydrogen was found as the temperature increased. Longfield (5) observed that at temperatures near 415° C a slow reaction which produces methanol (detected by a chemical method and by mass spectrometer) takes place. Increasing the surface to volume ratio by 35 times was reported to have a negligible effect on the rate, and the addition of inert gas (H_2) did not have any significant effect upon the amount of methanol formed. Klein (6) also

detected methanol using a mass spectrometer.

From experiments with formaldehyde without sensitizer, Longfield (5) calculated the rate constant for methanol formation on the basis of the integrated second-order equation assuming that the amount of formaldehyde disappearing is equal to twice the quantity of methanol formed. With initial pressures from 110 to 240 mm at 415° C, or lower, the value remained approximately constant indicating that the reaction is nearly second order. The order was also determined from a log-log plot of the rate of methanol formation and the average pressure of formaldehyde during a reaction. The order at 415° C calculated by this method is 1.7. Klein (6) confirmed these observations by observing that the rate of change of $P_{CO} - P_{H_2}$ follows second order kinetics. Comparison of the rate of formaldehyde consumption in baked and unbaked reaction vessels showed that less CH_3OH was formed in the faster total reactions in unbaked vessels. Klein interpreted this as "evidence that methanol arises from a non-chain, homogeneous process".

It is apparent that the pyrolysis of formaldehyde is so far not completely understood. A summary of the main points of interest and reasons for pursuing this study follows.

(i) The interpretations of the early experiments designed to detect hydrogen atoms, by Patat, as well as Steacie's (3) experiment with deutero compounds, are not in agreement with the results of Klein's isotopic tracer experiments.

(ii) Klein suggested that both initiation and termination in hydrogen formation happen at the wall. Longfield proposed that in the sensitized reaction the principal method of termination is in the gas phase.

(iii) Although Klein observed that less methanol is formed in the unbaked vessel in which formaldehyde is consumed faster and accepted this as indirect evidence that methanol is possibly formed by a non-chain reaction, Longfield discovered a sensitized reaction for methanol formation at 415° C.

(iv) In a study of the pyrolysis of dimethyl ether, Benson (8) used the CH_3O radical in his reaction mechanism. Furthermore, he suggested a possible participation of CH_3O radical in a chain propagating step for methanol formation in the pyrolysis for formaldehyde at 415° C.

(5) $CH_2O + HCO \rightarrow CH_2OH + CO$

(6) $CH_2OH + CH_2O \rightarrow CH_3OH + HCO$

which competes for HCO radical in the hydrogen producing chain

(3) $HCO + M \rightarrow H + CO + M$

(4) $H + CH_2O \rightarrow H_2 + HCO$

This proposal is quite interesting.

(v) Gay (9) detected the CH_3O radical in the homogeneous reaction producing H_2 and CO in shock waves.

(vi) In view of the possible large activation energy and low frequency factor for the four-centre reaction, the elementary molecular reaction of $CH_2O + CH_2O \rightarrow CH_3OH + CO$ to form methanol is unlikely. Besides, examples of four centre reactions are rare.

(vii) Eusuf and Laidler studied the thermal decomposition of acetaldehyde (10) and proposed a hydrogen transfer reaction

$$2CH_3CHO \rightarrow CH_3CO + CH_3CHOH,$$

as the initiation step. As a result of further work on acetaldehyde pyrolysis, however, Laidler and Liu abandoned the original idea and used the reaction

$$CH_3CHO \rightarrow CH_3 + CHO,$$

instead, as the chain initiating reaction. For a discussion of a Rice-Herzfeld mechanism see Benson (11). Gay (9) in his work on formaldehyde pyrolysis again used a hydrogen atom transfer reaction as the initiation step

$$CH_2O + CH_2O \rightarrow CH_2OH + HCO$$

in one proposed mechanism.

A thorough understanding of the pyrolysis of formaldehyde requires that data be obtained over a large temperature range using a variety of techniques. In the present work an attempt is made to contribute to the investigation of formaldehyde pyrolysis at 420° C where the products are mostly CH_3OH and CO and at 452° C where H_2 is also a major product. Besides, we would like to

propose a mechanism for methanol formation which could be combined with a hydrogen producing mechanism to obtain a complete mechanism for the pyrolysis for formaldehyde over a wide temperature range.

EXPERIMENTAL SECTION

1. Materials

(i) Formaldehyde Monomeric formaldehyde was generated from well dried paraformaldehyde by the method of Spence and Wild (12) by first evaporating to dryness a 40% solution of formaldehyde (McArthur Chemical Co. Ltd. Fl 4182 F3). The product was broken up, dried in a vacuum desiccator over sulfuric acid for 2 days, powdered, and placed in the distillation vessel (50 cm^3). A thick wad of glass wool was introduced to prevent particles of the solid from being carried over into the condensing system during the distillation. The vessel was sealed to the apparatus as shown in Figure 4.

The system was first pumped out by an oil-diffusion pump, and the condensing vessels heated with a Bunsen flame. Distillation was begun by heating the paraformaldehyde vessel to 110° C in an oil-bath. During the removal of the first fraction by the pump, the condensing vessels were heated gently with a gas torch. Since formaldehyde reacts rapidly with oxygen absorbed on glass at 300° C (13), the above treatment should be such as to effectively free the surface of oxygen. The trap was now cooled in liquid N_2, and the stop-cock leading to the pump was shut off. When sufficient solid had collected in the trap, the oil-bath was removed, the apparatus once more connected to the pump, and the trap sealed off from the separator. By

distillation twice from -78° to -196° C the CH_3OH was removed, so that none was detectable by VPC analysis, carried out as described below. Also, no water or other impurities were detectable by VPC analysis. The sample kept in a liquid nitrogen trap (-196°) and at a pressure of about 10^{-4} Torr could remain unpolymerized for around two months. No impurities could be detected by mass spectrometry, up to about m/e 80, except a small amount of m/e 60 which was probably dimer.

(ii) Methanol Commercial methanol, claimed to be 99.5% CH_3OH was used for calibration of the VPC. It was treated as a pure sample since 0.5% is small in comparison with the 3% experimental error of the VPC.

(iii) Carbon Dioxide Bone dry CO_2 from Matheson of Canada Ltd. was used without purification for calibration of the mass spectrometer. For the inert gas experiments the CO_2 was frozen and evacuated to 10^{-4} Torr to remove non-condensable gases.

2. Apparatus

(i) Reactor and Pressure Measurement Device The reactor was made of pyrex glass, of volume 1110 cm^3. Before using, it was cleaned with detergent, then rinsed many times with deionized water. For measuring pressure, a pyrex spoon gauge was used. The hollow end of the spoon gauge was attached to the reactor at one end and to a needle at the other. The motion of the needle was detected by means of the photo-transistor device described

by Paul Ke (14). See Figure 3 for a diagram of the apparatus. The smallest pressure change detected by the spoon gauge used before experiment # 24 was 0.02 cm of Hg and by that used after was 0.005 cm of Hg. A series of pressure readings of some gas in the reactor, taken successively over a period of 30 minutes, gave the result, with mean error, 11.40 ± 0.04 cm. The drift in the galvanometer was generally less than 0.1 cm in one half hour, equivalent to less than 0.05 cm of Hg.

The reactor described above is represented by R in Figure 1. The gauge is connected to one of the arms of the manometer M_1 and to a fore pump via a two-way stop-cock. The image of the needle was focused on two phototransistors, Figure 3, and the pressure read on manometer M_1.

First, the reactor and gauge were evacuated and the image of the needle was focused on the middle of the two phototransistors and the galvanometer reading was set to zero by means of the resistors. This was taken as the null position of the needle. A pressure of air equal to the required reactant pressure was leaked to the gauge side. This displaced the needle, and the galvanometer, from their null positions. Next the reactant was administered into the reaction vessel until the needle came back to the null position, i.e. the galvanometer returned to zero. For the measurement of pressures larger than 10 cm of Hg, this process had to be done in two or three steps

to prevent breakage of the spoon gauge.

(ii) Furnace The furnace, constructed and first used by P. Ke, consisted of an aluminum cylinder, wound with six chromel-A heaters in two layers of three. The outer three were regulated by means of a platinum probe and relay. The cylinder and heaters were insulated by asbestos and were kept in a 25 gallon steel drum containing vermiculite. For details see Figure 2.

(iii) Thermocouples Six calibrated thermocouples of chromel alumel were used to measure the temperature at the various points of the reactor. The thermocouples had already been calibrated by P. Ke. The results showed that the deviations were less than $0.22^{o}C$ compared with the table in the Handbook of Chemistry and Physics. No attempt was made for any corrections or to carry out further calibrations.

(iv) Temperature Control Temperature control was obtainable within $\pm 0.25^{o}C$. Typical readings (in millivolts) of six thermocouples were taken from run 13. Thermocouple # 5 was at the top of the neck of the reactor and # 6 was near the bottom of the neck. # 1 and # 2 were in the well (See Figure 5). The average of readings from # 1 to # 4 only was taken as experimental temperature.

(1)	(2)	(3)	(4)	(5)	(6)
17.232	17.238	17.239	17.239	2.902	17.202

Average = 17.237 or $419.93^{o}C$

(In this temperature range $1.00^{o}C$ is equivalent to 0.04 millivolt.)

(v) Vacuum System Except for a few modifications of the lines inside the hot box, the addition of a new reservoir F, and a new reactor R, most of the vacuum system was constructed by P. Ke (See Figure 4). The following accessories were used:

(a) Fore Pump

Welch Duo-Seal Serial No. 8698-3

(b) Diffusion Pump

VEECO Model No. EP 25W

(c) Thermocouple Pressure Gauge

C.V.C. GTC - 100

3. Introduction of Reactants

In those runs before # 22, formaldehyde was introduced directly into the reactor from the storage bulb. From run # 23 on formaldehyde was introduced first to a reservoir F, Figure 1, of volume 1153 cm^3, inside the hot box, in which the pressure was measured, then expanded into the reactor. With the latter method, the pressure in the reactor obtained from calculation has been shown by direct measurement to be less than 1.0% in error. An electric fan was used to circulate the air inside the hot box in an attempt to keep all the parts in the hot box at 80^o C, to prevent polymerization of formaldehyde. However, the temperatures near the spoon gauge and VPC volume S were found to be around 20^o lower. In the experiments with inert gas, formaldehyde of known pressure was introduced first to the reservoir F (Figure 1),

followed by the inert gas CO_2, keeping the pressure of CO_2 higher than the total pressure of CH_2O and CO_2 inside the reservoir until the required pressure had been reached. The two gases were let stand for 30 minutes to ensure complete mixing, then expanded to the reactor. Time measurement followed immediate closure of stop-cock T_{15}, and the pressure change due to reaction was followed. Except for the experiments with inert gas, the formaldehyde sample outside the reactor was returned to Sg.

4. Analytical Procedures

All the volumes between stop-cocks T_{18}, T_{16}, T_{14}, T_{12}, T_7; T_{12}, T_{43}; T_{29}, T_2; T_2, T_{23}; T_{23}, T_{22}, T_{24}; and volumes Sg, S, F, V_1, and R are known. At the end of the reaction time, stop-cock T_{15} was opened immediately, and the contents of the reactor were expanded to the line between stopcock T_{19}, T_7, T_{11}, T_{12}, T_{14}. Thus part of the products was introduced into VPC volume S. Stopcock T_{18} was then closed and T_{14} opened to remove non-condensable products. The volume of part of the non-condensable products was measured by pumping off the gases with an automatic toepler pump into the calibrated section of the manometer M_2.

The condensable products which were collected in Trap C at -196°C were discarded. The products collected in VPC volume S were used for condensable products analysis by means of the gas phase chromatograph.

In some of the runs, part of products was collected from stopcock T_{41} for mass spectrometric analysis. During these runs, products were introduced into the sampling line between stopcock T_{12} and T_{43} by opening stopcock T_{12} before opening T_{14} and after closing T_{18}.

5. Vapor Phase Chromatographic Analysis

The apparatus used was a Dynatronic Instrument Chromalyzer-100 Gas Chromatograph with a thermal conductivity cell detector.

The columns were prepared from 18.5 feet lengths of 1/4-inch copper tubing, coiled, after packing, to fit the instrument. The solid support used was chromosorb W (Johns-Manville Products Corp.) boiled for 1 hour in glacial acetic acid and water washed before coating. The liquid phase used for analysis was Ethofat 60/25 (Armour Industrical Chemical Co.).

100 ml (34 grams) of chromosorb was coated with 6.8 g Ethofat by dissolving the latter completely in 25 cm^3 of hot chloroform, mixing with the chromosorb, and then drying completely at room temperature. The column was then packed with dry chromosorb as quickly as possible. After the column was attached to the apparatus it was heated to 150° C and a flow of helium established for 24 hours to sweep out all fractions of the phases which are volatile at operating temperature.

The VPC volume S, see Figure 1, is a known volume. The sample or products to be analyzed could be expanded to this volume

when it was evacuated, from the line in the hot box, or directly from reactor R by opening stopcock T_{18}. This sample in turn could be transferred to the chromatographic apparatus by turning stopcock T_{19}.

Helium, under a gauge pressure of 9.5 pounds per square inch, was used as carrier gas. The flow rate was 50 ml per minute in the sample line and 25 ml per minute in the reference line at the operating temperature. High chart speed was used to obtain a more accurate measurement of peak area. Detector filament current was kept at 220 milli-amperes and operating temperature was adjusted to maintain around 120° C for those runs before # 48 and around 100° C afterward. A better separation of formaldehyde and methanol was obtained at 100° C. Bombaugh and Bull (15) also obtained a better separation at lower temperature.

The least amount of sample which could be detected by the method is thought to be reliable to around 3%. However, due to trouble encountered, i.e. the overlap of peaks of formaldehyde and methanol, in some of the runs the standard deviation by VPC analysis went to as high as 6%.

6. Material not Condensable in the Liquid Nitrogen Trap

The quantity of gas which was not condensable at -196° C was measured by reading the pressure it exerted in a portion of the calibrated volume. This product was completely combusted

over copper oxide at 260° C (according to the equations $2CO + O_2 \rightarrow 2CO_2$ and $2H_2 + O_2 \rightarrow 2H_2O$) between stopcock T_{24} and T_{25}, see Figure 1. This gas was completely condensed at liquid nitrogen temperature. Therefore, by putting a liquid nitrogen trap at A_2, Figure 1, complete combustion of gas and leakage of the vacuum system could be tested. By replacing the liquid nitrogen trap with a dry ice trap (a C_2H_5OH slush bath was used instead of dry ice since run # 50) CO_2 would evaporate into the vacuum line. Again CO_2 was collected in the calibrated volume by Toepler pump and the amount of CO could be calculated. By subtracting the quantity of CO from the total amount of non-condensable gas the quantity of H_2 could also be calculated.

7. Mass Spectrometric Analysis

In runs # 37, 38, 39, 40, 41, 48, 49, 50 products were taken from T_{41} for mass spectrometric analysis. The apparatus used was modified from a Type 21-614 Residual Gas Analyzer (Consolidated Electrodynamics Corporation). The background pressure was 1.30×10^{-7} to 1.40×10^{-7} Torr. The ionizing current was fixed at 30 micro-amperes; input sensitivity at "high" and scan rate at 5. In the inlet system the optimum pressure inside the metering volume (approximately 10 cm^3) was 2 cm Hg. After expanding this volume to a reservoir of 2 liters volume, the pressure was reduced to 10^{-1} Torr, which would establish a pressure of about 10^{-4} Torr inside the ionizing chamber through the gold leak.

8. Calibration of Vapor Phase Chromatograph

Calibration for both CH_2O and CH_3OH was carried out at operating conditions for VPC analysis. Pure formaldehyde (prepared as described above) was introduced into the line in the hot box. With the VPC volume S, Figure 1, connected to the spoon gauge, the pressure in the VPC volume S could be read directly. Four runs of CH_2O with pressure ranging from 62.1 mm Hg to 97.6 mm Hg, which are equivalent to 0.390 μmole to 0.611 μmole in VPC volume at around 120° C, were done. The plot, see Figure 10, of μmole in VPC volume against peak area was obtained. The calibration chart uses areas adjusted to that obtainable using attenuation 8. The calibration of the methanol was done in the same way except that in order to obtain a very low pressure beyond the accuracy of the mercury manometer used with spoon gauge, the methanol was first collected in the spoon gauge volume only, while the rest of the line inside the hot box was evacuated. It was then expanded from the spoon gauge to the line and VPC volume S. The pressure thereafter and the number of μmoles of methanol inside the spoon gauge could be calculated. The calibration chart of methanol is shown in Figure 11. In the VPC calibration for CH_3OH the spoon temperature was, however, found afterward to be 20° C lower than the hot box temperature, which in turn will result in a -6% in error of calibration; therefore, a correction of +6% was made. This correction also brought the sensitivities of CH_2O and CH_3OH in VPC to be exactly the same, which is in good agreement with their similar heat conductivity.

9. Dead Space in the Reactor

The spoon gauge was used to measure the pressure change in the reactor for runs # 9 - 22. From run # 23 the spoon gauge was only used for measuring the formaldehyde pressure in the reservoir F, Figure 1, before expanding to the reactor. The spoon gauge was isolated from the reactor while the reaction was in progress during these runs. At the end of the reaction time for runs # 9 - 22, stopcock T_{17}, Figure 1, was closed to disconnect the spoon gauge and reactor to prevent a sudden change of pressure in the spoon gauge when the reaction products were removed from the reactor. The gas in the reactor only was taken for analysis. This was based on the assumption that the gases would diffuse so slowly between spoon gauge and the reactor, due to the capillary connection that the gas inside the spoon gauge,whose temperature was only 80^{o} C, was considered not to react. As to the reactor itself, a dead space amounting to about 10 ml was maintained at 80 - 100^{o} C. This will cause an error of -1 to -2% in the estimated reaction rate. It is small compared to the experimental error; therefore, no correction was made.

RESULTS

1. Products

The products of two long reaction time experiments at 420° C and another two at 452° C are shown in Table I. The exact match between the quantity of CH_3OH from vapor phase chromatographic analysis with that calculated, i.e. $n_{CH_3OH} = n_{CO} - n_{H_2}$, indicated that there were no reactions producing CO other than the two reactions

$$\text{I.} \quad CH_2O \rightarrow H_2 + CO$$

$$\text{II.} \quad 2CH_2O \rightarrow CH_3OH + CO$$

Similar data for short reaction times at both 420° C and 452° C are also listed in Tables II and III. Due to the overlap of the methanol and formaldehyde peaks, the vapor phase chromatographic analysis of methanol was not as accurate as would be desired. However, the quantity of methanol obtained by analysis and that obtained by subtracting the quantity of H_2 from the quantity of CO differ in most cases only by the experimental error in analysis, for both long and short reaction times. It was, therefore, concluded that $n_{CO} - n_{H_2}$ is a reliable estimate of the methanol formed. This assumption was also made by Klein (6). The orders of reaction were obtained using both methods, and do not differ appreciably.

Although the data for formaldehyde remaining at the

end of the reaction were available from vapor phase chromatographic analysis the analyses for the small amount of formaldehyde disappearing which represent the difference between two large quantities (initial amount - unreacted material) are not of great reliability; therefore, the total balance of carbon was not reliable for initial rate experiments. However, the results of experiments # 49, # 50 at 452° C show that in the long reaction time experiments, in which formaldehyde was completely pyrolyzed, a good total balance of carbon was obtained. This is evidence that no third reaction is involved in pyrolysis of formaldehyde under these conditions, at least at the end of the reaction. Recall that both Fletcher and Klein found evidence for a third reaction.

Mass spectrometric analyses of the reactor contents in both initial rate and long time reactions were consistent with the presence of formaldehyde, methanol and carbon monoxide. Small peaks at mass number 60 and 76 were also found. The peak at m/e 60 was possibly the dimer of formaldehyde and that at m/e 76 could be $HCOOCH_2OH$, a product from reaction of formaldehyde and a small impurity of HCOOH. Carruthers and Norrish (16) found that this reaction occurred readily in the presence of small amounts of HCOOH.

2. Effect of Reactor History

The reactor was never exposed to the air after

experiment # 4, and it was isolated from the system while not in use. Before each run the reactor was conditioned by pumping with the oil diffusion pump to below 5 x 10^{-3} mm Hg.

From Tables II and III one can observe that the rate of formation of H_2 is less in experiments # 30, 31, 34, 36, and 37 than in experiments # 9 - 17. This possibly indicates that the rate of formation of H_2 is dependent upon the condition of the reactor surface. There is no apparent change in the rate of formation of CH_3OH in the same set of experiments. At the same temperature but in a different reactor Ke reported that the rate of H_2 formation was decreased considerably when the reactor was pumped with the oil diffusion pump for 24 hours instead of one hour only. Two successive runs with different hours of conditioning (in # 11 the reactor had been pumped by the oil diffusion pump for 20 hours before the run started while in #12 it was pumped for 3 hours only) in the present work, however, showed no significant difference in the reaction rate.

3. Effect of Adding Inert Gas CO_2

Experiments at both 420° C and 452° C showed that the addition of 100 mm Hg of carbon dioxide increased the rate of hydrogen formation, but had no effect upon the rate of methanol formation. Figure 6 and Figure 8 have these effects clearly shown.

4. Induction Period in Hydrogen Formation at 452° C

In Figure 9 a plot of the amount of hydrogen formed against reaction time showed that there was no sign of an induction period in hydrogen formation at this temperature, although the data are quite scattered.

5. Orders of Reaction and Activation Energy Calculation

In Figures 6, 7, and 8 the logarithm of initial rate of formation of methanol and hydrogen at both 420° C and 452° C have been plotted against the logarithm of initial concentration of formaldehyde. The initial concentrations of formaldehyde were used here, because in the initial rate reactions the concentration of formaldehyde was changed by only about 5%. When the logarithm of formaldehyde concentration was taken this 5% difference would only cause a shift (raise) of the position of the straight line. Although the Y-intercept would be changed, the slope of the straight line would remain exactly the same. Furthermore, the distance between the intersection of two straight lines with Y axis, which could be used for activation energy calculation, would also remain unchanged. The orders of reaction were calculated, with an IBM 1620 computer, using the least squares treatment. The results are as follows:

Reaction Orders

	420°	452°
Methanol	1.82 ± 0.05[a]	2.09 ± 0.06[a]
	1.87 ± 0.04[b]	2.08 ± 0.08[b]
Hydrogen	2.09 ± 0.16	2.43 ± 0.18

where (a) is the result of the calculation using the equation $n_{CH_3OH} = n_{CO} - n_{H_2}$ and (b) is from VPC analysis. The difference in reaction orders of methanol between two different temperatures might be caused by some systematic experimental error. However, we could conclude from these data that although the reaction is nearly second order, a variation in order with temperature is suggested. Longfield (5) at 415° C also proposed that the reaction was nearly second order; however, the order calculated by him by one method is 1.7. The apparent variation with temperature is interesting.

An Arrhenius plot for the activation energy calculation requires data from at least three different temperatures. Since experiments at only two different temperatures had been done in the present work, the activation energy was evaluated by means of the following equation.

$$\log \frac{k_1}{k_2} = \frac{E_a}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2} \right) \qquad (A)$$

Assume that the rate expression is of the form

$$\frac{d(CH_3OH)}{dt} = k(CH_2O)^x,$$

thus $$\log\frac{d(CH_3OH)}{dt} = \log k + x\log (CH_2O).$$

The above equation has been plotted in Figures 6 and 7 with $\log \frac{d(CH_3OH)}{dt}$ on the Y axis and log (CH_2O) on the X axis. The slope P represents the order for methanol formation and the intersection on the Y axis represents the logarithm of the rate constant. Thus $\log \frac{k_1}{k_2} = \log k_1 - \log k_2$ is the distance between the two Y intercepts from data at two temperatures. This value is also equal to the vertical distance between these two straight lines, and would be the same taken from everywhere if the slopes of these two lines were the same. However, as indicated above, due to some systematic experimental error, or a change in order with temperature, the orders of reaction at both temperatures were not exactly the same. As a result, the distance between two Y-intercepts would differ considerably from the vertical distance between two straight lines taken at the region where these experiments were done. Therefore, the region equivalent to a starting pressure of formaldehyde of 130 mm Hg was used. There are two reasons for this treatment: first, this is the highest pressure used, hence the experimental

error, i.e. in pressure measurement and product analysis, would be the least; second, the majority of experiments was done at this starting pressure. Thus from Figure 6

$$\log k_1 - \log k_2 = 0.43$$

Substituting this value into equation (A) gives

$$E_a = 30.9 \text{ Kcal mole}^{-1}.$$

This is in good agreement with the value of 31 K cal mole^{-1} obtained by Longfield (5). By the same argument the activation energy of hydrogen formation could also be evaluated,

$$E_a = 38.8 \text{ Kcal mole}^{-1}.$$

This value is slightly lower than Fletcher's (1) report of 44.5 Kcal mole^{-1} and greater than Gay's (9) report of 28 Kcal mole^{-1}.

6. Preexponential Factor Calculations

The preexponential factor of the rate constant k for methanol formation was calculated by taking one point from Figure 7 equivalent to a formaldehyde pressure of around 128 mm Hg and substituting into

$$\frac{d(CH_3OH)}{dt} = k(CH_2O)^n ,$$

assuming the order to be two. At 420° C, $\log \frac{d(CH_3OH)}{dt} = -7.13$ and $\log (CH_2O) = -2.51$ giving

$$k = 7.76 \times 10^{-3} \text{ 1 mole}^{-1}\text{sec}^{-1}.$$

Also from Arrhenius equation $k = A\exp(-E/RT)$,

$$\log_{10} A = 7.62$$

and $$A = 4.17 \times 10^{+7} \text{ 1 mole}^{-1} \text{ sec}^{-1}$$

or $$4.17 \times 10^{10} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

With the same method we can also obtain 4.9×10^{10} cc mole^{-1} sec^{-1} at 452° C. This again is in good agreement with Longfield's (5) result of $0.9 \times 10^{8} T^{1/2}$, 1 $\text{mole}^{-1}\text{min}^{-1}$ which will yield value of 3.93×10^{10} and 4.02×10^{10} cc $\text{mole}^{-1}\text{sec}^{-1}$ at 420° C and 452° C respectively.

DISCUSSION

1. Review of Mechanisms Suggested in the Radical Sensitized and Thermal Decomposition of Formaldehyde

The kinetics and surface effects as well as the inert gas effects of the radical sensitized decomposition of CH_2O were carefully studied by Longfield and Walters using ethylene oxide as a source of methyl radicals. The chain initiating reactions were considered to be

$$(CH_2)_2O \rightarrow CH_3 + HCO$$

$$CH_3 + CH_2O \rightarrow CH_4 + HCO\ .$$

A reaction chain, which accounts for the formation of hydrogen and carbon monoxide, is established by reactions (3) and (4).

$$(3)\quad HCO + M \rightarrow H + CO + M$$

$$(4)\quad H + CH_2O \rightarrow H_2 + HCO$$

M is either a foreign gas or CH_2O. After comparing the reaction rates in packed and unpacked vessels, and with and without added gas, they suggested that in the unpacked vessel the principal method of termination was the gas phase (homogeneous) reaction,

$$(7)\quad HCO + HCO \rightarrow \text{products}$$

In a packed vessel the rate expression was consistent with the wall termination reaction,

$$HCO \xrightarrow{\text{wall}} \text{products}$$

If the life-time of HCO radical in the gas phase is not too long

and the rate of diffusion of HCO to the wall is inhibited by CH_2O or M, the rate of the termination reaction could be decreased by inert gas (7). The rate of the over-all decomposition would be increased, as observed, and reaction (3a) could be used.

(3a) $HCO \rightarrow H + CO$

The accelerating effect of inert gas could also be through reaction (3), a third body effect; or the inert gas could affect the surface so as to inhibit chain termination (5). However, at moderate pressures reaction (3) is likely to be in the second order region (17) as is therefore preferred.

Although Longfield, comparing the rate of methanol formation with and without the sensitizer ethylene oxide, found that the rate of methanol formation at 415°C was larger in the presence of 2mm of ethylene oxide than in the case of pure formaldehyde (120 mm), and those in the presence of more ethylene oxide being even slightly higher; since CH_3OH was not a major product no mechanism was proposed.

Klein, Scheer and Schoen (6) based their mechanism for the pyrolysis of formaldehyde on the suggestion of Calvert and Steacie (7) that chain termination in the photolysis of CH_2O happens at the wall. From the results of their own pyrolysis experiments in the baked and unbaked reaction vessels, i.e. the rate is dependent upon the vessel condition but not on the S/V ratio, they concluded that both chain initiation and termination

are wall reactions. The reaction suggested for chain initiation is

$$(1a) \quad CH_2O + CH_2O \xrightarrow{\text{wall}} HCO + H + CH_2O,$$

which could be interpreted as either collision of a gas phase CH_2O molecule with the CH_2O molecules adsorbed on the wall or reaction between two adsorbed CH_2O molecules. The chain propagating steps (3a) and (4) were the same as used by Longfield and Walters,

$$(3a) \quad HCO \rightarrow H + CO$$

$$(4) \quad H + CH_2O \rightarrow H_2 + HCO$$

except that the inert gas effect which is expected in reaction (3) was not taken into consideration. The chain terminating step (7a), which was proposed is the same as suggested for the radical sensitized reaction in packed vessels (5).

$$(7a) \quad HCO \xrightarrow{\text{wall}} \text{products}$$

Gay, Glass, Kistiakowsky, and Niki (9), in their study of the homogeneous pyrolysis of formaldehyde to H_2 and CO in shock waves, detected the radical H_3CO and observed a low activation energy of 28 ± 2.5 kcal $mole^{-1}$. Three radical chain mechanisms were proposed, one of which accounted for the presence of CH_3O;

$$(1) \quad 2\ CH_2O \rightarrow H_2COH + HCO$$

$$(3) \quad HCO + M \rightarrow H + CO + M$$

$$(2) \quad H_2COH + M \rightarrow H_2 + HCO + M$$

$$(4) \quad H + CH_2O \rightarrow H_2 + HCO$$

$$(7) \quad 2\ HCO \rightarrow 2\ CO + H_2$$

The rate expression is

$$-\frac{d(CH_2O)}{dt} = k_4 (H)\ (CH_2O) = k_3\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (M)(CH_2O)$$

The estimated activation energy was 48 kcal $mole^{-1}$. This value, although much higher than their observation of 28 kcal is closer to the experimental activation energy of 38.8 kcal in present work. In this mechanism, the chain initiating reaction (1) accounts for the observation of H_2COH radical. Reaction (2) is a pressure dependent reaction considered as part of the chain initiation step. Both of the chain propagating steps (3) and (4), and terminating step (7) are the same as those proposed by Longfield for unpacked vessels. This mechanism accounts for the rate expression found

$$-\frac{d(CH_2O)}{dt} = k(CH_2O)\ (Ne)$$

Although Klein (6) suggested that initiation and termination in the thermal decomposition are wall effects, Longfield (5), in their study of the radical-sensitized decomposition of formaldehyde, concluded that surface reactions were not important in the unpacked vessels.

2. Methanol Formation

The reactions which lead to the formation of CH_3OH and of H_2 are in some way independent, because of the observations that addition of inert gas has an effect on the rate of H_2 formation but not on the rate of methanol formation and that hydrogen formation is quite erratic and methanol formation is not

(see Table II). These observations are similar to those of Klein who found that rates of H_2 formation are sensitive to the history of the reaction vessel. As discussed in the introduction, a four-centre hydrogen atom transfer reaction seems unlikely. In view of the involvement of CH_2OH and HCO radicals in the reaction it is also difficult to find a non-chain radical mechanism. Therefore, a mechanism for the formation of CH_3OH will first be discussed, assuming temporarily that the mechanisms for the formation of H_2 and of CH_3OH are independent.

If we use Gay's chain initiation step for hydrogen formation

$$(1) \quad CH_2O + CH_2O \rightarrow CH_2OH + HCO$$

and the chain propagating reactions proposed by Benson (8)

$$(5) \quad HCO + CH_2O \rightarrow CH_2OH + CO$$

$$(6) \quad CH_2OH + CH_2O \rightarrow CH_3OH + HCO$$

with a suitable termination reaction, a simple Rice-Herzfeld scheme is obtained. According to Goldfinger, Letort, and Niclause (18) (see discussion by Laidler (19)), in a second order overall reaction, with a second order initiation, the termination reaction should be of the $^{\beta\beta}$type. In this case reaction (7) (7a) or (7b) could be termination reactions.

$$(7) \quad HCO + HCO \rightarrow CH_2O + CO$$

$$(7a) \quad HCO + CH_2OH \rightarrow CH_3OH + CO$$

$$(7b) \quad CH_2OH + CH_2OH \rightarrow CH_3OH + CH_2O$$

All of these reactions are bimolecular hydrogen atom exchange

reactions and have heats of reaction of -49, -57, and -51 kcal respectively. Therefore, their activation energies may be low and approximately the same. If the assumption is made that $E_7 \approx E_{7a} \approx E_{7b}$, the rate constants will be determined largely by the frequency factors, which depend upon the relative complexities of the molecules, the more complex the reactant molecules, the smaller the frequency factor obtained (20). Simple collision theory predicts preexponential factors of bimolecular reactions to be about 10^{14} cc $mole^{-1} sec^{-1}$, but the steric factors of bimolecular reactions show a decrease as the complexity of the reacting species increase (21). Also the transition-state theory allows the same prediction to be made (21). Therefore, the preexponential factors are probably in the order

$$HCO + HCO > HCO + CH_2OH > CH_2OH + CH_2OH$$

and reaction (7) may be selected. However, the problem is more complicated because the termination step depends upon the radical concentration which depends upon k_5 and k_6 as well as on the termination rate constants. Reaction (7) which was suggested by Longfield, is used, although the others might also be important. The mechanism is:

Chain initiation:

$$(1) \quad CH_2O + CH_2O \rightarrow CH_2OH + HCO \qquad \Delta H = 43 \text{ kcal}$$

Chain propagation:

$$(5) \quad HCO + CH_2O \rightarrow CH_2OH + CO \qquad \Delta H = -11 \text{ kcal}$$

$$(6) \quad CH_2OH + CH_2O \rightarrow CH_3OH + HCO \qquad \Delta H = -8 \text{ kcal}$$

Chain Termination:

$$(7) \quad HCO + HCO \rightarrow CH_2O + CO \qquad \Delta H = -49 \text{ kcal}$$

The rate equations are

$$-\frac{d(CH_2O)}{dt} = 2k_1(CH_2O)^2 + k_5(HCO)(CH_2O) + k_6(CH_2OH)(CH_2O) - k_7(HCO)^2 ,$$

$$\frac{d(HCO)}{dt} = k_1(CH_2O)^2 - k_5(HCO)(CH_2O) + k_6(CH_2OH)(CH_2O) - 2k_7(HCO)^2 ,$$

$$\frac{d(CH_2OH)}{dt} = k_1(CH_2O)^2 + k_5(HCO)(CH_2O) - k_6(CH_2OH)(CH_2O) ,$$

$$\frac{d(CO)}{dt} = k_5(HCO)(CH_2O) + k_7(HCO)^2 ,$$

and $$\frac{d(CH_3OH)}{dt} = k_6(CH_2OH)(CH_2O).$$

Application of the stationary state treatment gives

$$k_1(CH_2O)^2 - k_5(HCO)(CH_2O) + k_6(CH_2OH)(CH_2O) - 2k_7(HCO)^2 \cong 0,$$

$$k_1(CH_2O)^2 + k_5(HCO)(CH_2O) - k_6(CH_2OH)(CH_2O) \cong 0,$$

and $$HCO = \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O).$$

If it is assumed that the chains are sufficiently long (that is > 10) the initiation and termination steps may be neglected in comparison with the chain propagating steps

$$k_5(HCO)(CH_2O) - k_6(CH_2OH)(CH_2O) = 0$$

and $$(CH_2OH) = \frac{k_5}{k_6}\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O).$$

The rate expressions are

$$-\frac{d(CH_2O)}{dt} = 2\,k_5\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)^2 ,$$

$$\frac{d(CO)}{dt} = k_5\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)^2$$

and $$\frac{d(CH_3OH)}{dt} = k_5\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)^2$$

The activation energy $\Delta E = E_5 + \frac{1}{2} E_1 - \frac{1}{2} E_7$ can be estimated from the following considerations. Reaction (1) is endothermic by about 43 kcal (9). As discussed by Gay, Glass, Kistiakowsky

and Niki, the reverse reaction, involving two free radicals, should have a low activation energy which may be set equal to that of a similar reaction (7). Therefore,

$$\frac{1}{2}(E_1 - E_7) \simeq \frac{1}{2}\Delta H_1,$$

Also, reaction (5) is very similar to reaction (4),

$$(4) \quad H + CH_2O \rightarrow H_2 + HCO$$

which has an activation energy of ≤ 5.7 (6), (22). Thus we can expect an activation energy of around 6 for reaction (5). Then

$$\Delta E_{calc.} = 6 + \frac{1}{2}\Delta H_1 = 6 + \frac{43}{2} = 28 \text{ kcal.}$$

The mechanism suggested satisfies the following observations:

(i) The reaction is second order.

(ii) There is no inert gas effect.

(iii) Reactions (1), (5), and (7) are written as homogeneous reactions accounting for the independence of the rate of S/V ratio (5) and the apparent insensitivity to vessel history.

(iv) The estimated activation energy is very close to the experimental activation energy, 30.9 kcal.

(v) The frequency factor 4×10^{10} cc mole^{-1} sec^{-1} is normal for a bimolecular reaction, which in this case would be A_5 if $A_1 \simeq A_7$,

$$A = A_5 \left(\frac{A_1}{A_7}\right)^{\frac{1}{2}} \simeq A_5$$

If reaction (7a) is used as the chain termination step a mechanism can also be written as follows:

(1)	$CH_2O + CH_2O \rightarrow CH_2OH + HCO$	$\Delta H = 43$ kcal
(5)	$HCO + CH_2O \rightarrow CH_2OH + CO$	$\Delta H = -11$ kcal
(6)	$CH_2OH + CH_2O \rightarrow CH_3OH + HCO$	$\Delta H = -8$ kcal
(7a)	$HCO + CH_2OH \rightarrow CH_3OH + CO$	$\Delta H = -57$ kcal

This mechanism, with the assumption of long chains, leads to the expression

$$\frac{d(CH_3OH)}{dt} = \left(\frac{k_1 k_5 k_6}{k_{7a}}\right)^{\frac{1}{2}} (CH_2O)^2$$

Which is again of the correct kinetic form and will give the same activation energy, assuming that activation energies of reaction (5) and reaction (6) (both of them are reactions between a radical and a molecule to yield a radical and a molecule) are approximately equal. In this mechanism both reactions (5) and (6) are involved in the rate expression, instead of reaction (5) only as in the previous mechanism.

A third mechanism is also to be considered, in view of the possibility of reaction (7b) as a termination step.

(1)	$CH_2O + CH_2O \rightarrow CH_2OH + HCO$	$\Delta H = 43$ kcal
(5)	$HCO + CH_2O \rightarrow CH_2OH + CO$	$\Delta H = -11$ kcal
(6)	$CH_2OH + CH_2O \rightarrow CH_3OH + HCO$	$\Delta H = -8$ kcal
(7b)	$CH_2OH + CH_2OH \rightarrow CH_3OH + CH_2O$	$\Delta H = -51$ kcal

Again, assuming long chains, the expression

$$\frac{d(CH_3OH)}{dt} = k_6 \left(\frac{k_1}{k_{7b}}\right)^{\frac{1}{2}} (CH_2O)^2$$

is obtained. With the assumption used before, that $E_5 \simeq E_6$, the activation energy is almost the same as that given by the first mechanism. Reaction (6) is expected to have a lower pre-exponential factor than reaction (5), if $E_5 \simeq E_6$; then k_6 should be less than k_5 and the concentration of CH_2OH should be large, favouring the termination reaction (7b). However, based on the argument given before for termination reactions, reaction (7), hence the first mechanism is selected.

3. Complete Mechanism

In the temperature range of this study H_2, as well as CH_3OH, is a major product. Therefore, it is necessary to have a complete mechanism consistent with the observations on H_2 formation. By combining mechanism 1 (above) for methanol formation with Gay's mechanism (9) the following is obtained. Thermodynamic data was obtained from references (9) and (23).

(1)	$2CH_2O \rightarrow CH_2OH + HCO$	ΔH = 43 kcal
(2)	$CH_2OH + M \rightarrow H_2 + HCO + M$	ΔH = 9 kcal
(3)	$HCO + M \rightarrow H + CO + M$	ΔH = 26 kcal
(4)	$H + CH_2O \rightarrow H_2 + HCO$	ΔH = -25 kcal
(5)	$HCO + CH_2O \rightarrow CH_2OH + CO$	ΔH = -11 kcal
(6)	$CH_2OH + CH_2O \rightarrow CH_3OH + HCO$	ΔH = - 8 kcal
(7)	$HCO + HCO \rightarrow CH_2O + CO$	ΔH = -49 kcal

Reaction (1) is the chain initiation step; reaction (2) is also part of the chain initiation step. Reactions (3) and (4) are chain propagating steps for hydrogen formation, while reactions (5) and (6) are chain propagating steps for methanol formation. There is also a possibility of forming a chain between reactions (5) and (2) forming hydrogen; but since reaction (6) is expected to have a lower activation energy than reaction (2) (due to the fact that the heat of reaction of (2) is 17 kcal greater than that of (6)), a (5) - (6) chain is more probable than a (5) - (2) chain. Reaction (7) is the chain termination reaction. The steady-state equations are now, for the CH_2OH, HCO and H radicals,

$$k_1(CH_2O)^2 - k_2(CH_2OH)(M) + k_5(HCO)(CH_2O) - k_6(CH_2OH)(CH_2O) = 0,$$

$$k_1(CH_2O)^2 + k_2(CH_2OH)(M) - k_3(HCO)(M) + k_4(H)(CH_2O) - k_5(HCO)(CH_2O) + k_6(CH_2OH)(CH_2O) - 2k_7(HCO)^2 = 0$$

and $$k_3(HCO)(M) - k_4(H)(CH_2O) = 0$$

which can be solved to give

$$(HCO) = \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)$$

and

$$(H) = \frac{k_3}{k_4}\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (M).$$

Again, applying the long chain assumption, reactions (1) and (7) would be very slow in comparison with reactions (3), (4), (5) and (6). Therefore, the first equation can be simplified to

$$-k_2(CH_2OH)\ (M) + k_5\ (HCO)(CH_2O) - k_6(CH_2OH)(CH_2O) = 0$$

giving

$$(CH_2OH) = \frac{k_5\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}}\ (CH_2O)^2}{k_2\ (M) + k_6\ (CH_2O)}\ .$$

The rate equations

$$-\frac{d(CH_2O)}{dt} = 2\ k_1(CH_2O)^2 + k_4(H)(CH_2O) + k_5(HCO)(CH_2O) + k_6(CH_2OH)(CH_2O) - k_7(HCO)^2,$$

$$\frac{d(CO)}{dt} = k_3(HCO)(M) + k_5(HCO)(CH_2O) + k_7(HCO)^2,$$

$$\frac{d(H_2)}{dt} = k_2(CH_2OH)(M) + k_4(H)(CH_2O),$$

and $$\frac{d(CH_3OH)}{dt} = k_6(CH_2OH)(CH_2O),$$

may be simplified to the following equations using the long

chain assumption.

$$-\frac{d(CH_2O)}{dt} = k_4(H)(CH_2O) + k_5(HCO)(CH_2O) + k_6(CH_2OH)(CH_2O)$$

$$\frac{d(CO)}{dt} = k_3(HCO)(M) + k_5(HCO)(CH_2O)$$

$$\frac{d(H_2)}{dt} = k_2(CH_2OH)(M) + k_4(H)(CH_2O)$$

$$\frac{d(CH_3OH)}{dt} = k_6(CH_2OH)(CH_2O)$$

Using the expression for (HCO), (H), and (CH_2OH), the following rate expressions are obtained:

$$-\frac{d(CH_2O)}{dt} = k_3\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}}(M)(CH_2O) + k_5\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}}(CH_2O)^2 + \frac{k_5k_6\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}}(CH_2O)^3}{k_2(M) + k_6(CH_2O)}$$

$$\frac{d(CO)}{dt} = k_3\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}}(M)(CH_2O) + k_5\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}}(CH_2O)^2$$

$$\frac{d(H_2)}{dt} = k_3\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}}(M)(CH_2O) + \frac{k_2k_5\left(\frac{k_1}{k_2}\right)^{\frac{1}{2}}(CH_2O)^2(M)}{k_2(M) + k_6(CH_2O)}$$

$$\frac{d(CH_3OH)}{dt} = \frac{k_5 k_6 \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)^3}{k_2(M) + k_6(CH_2O)}$$

In order for the rate of CH_3OH formation to be independent of inert gas pressure and of order two, we must set $k_6(CH_2O)/k_2(M) \geq 5$.

(As mentioned before reaction (6) is expected to have a smaller activation energy than reaction (2), hence k_6 would be larger than k_2). The experimental errors are such that if k_2 were larger in relation to k_6 than shown, an inert gas effect would be detectable in methanol formation. It is suggested that in any further study a more accurate method be used for CH_3OH analysis and a wider range of inert gas pressure be tested. The rate of methanol formation will be

$$\frac{d(CH_3OH)}{dt} = k_5 \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)^2,$$

and the rate of hydrogen formation will be

$$\frac{d(H_2)}{dt} = k_3 \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)\ (M) + \frac{k_2 k_5}{k_6} \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (CH_2O)\ (M)$$

The rate expressions obtained above are consistent with the results of this study but cannot account for some of the results of Klein and of Ke.

As mentioned earlier, the rate of formation of H_2 is sometimes erratic, changing by up to a factor of two between experiments, while the rate of CH_3OH formation is quite reproducible. It is suggested that the erratic rate of formation of H_2 is caused by an erratic surface reaction, affecting reaction (6), which would result in a low rate of hydrogen formation when heterogeneous reaction (6) is rapid. By allowing k_2/k_6 to vary from 1/5 to smaller values, $d(H_2)/dt$ could vary from $k_3(\frac{k_1}{k_2})^{\frac{1}{2}}(M)(CH_2O) + \frac{1}{5} k_5(\frac{k_1}{k_7})^{\frac{1}{2}}(M)(CH_2O)$ down to $k_3(\frac{k_1}{k_7})^{\frac{1}{2}}(M)(CH_2O)$ if $k_2/k_6 \simeq 0$, i.e. k_6 is large. The allowed variation is from $\frac{1}{5}\, d(CH_3OH)/dt$ to zero ($(M) \simeq (CH_2O)$ if no inert gas is added). This is perfectly consistent with the results; see the groups of experiments 12 to 17, 18 to 20, 24 to 26, 45 to 47, and 53 and 54 in Tables II and III. If in # 15 and 16, for example, it is assumed that the low rate is mainly due to the homogeneous reaction $k_3(\frac{k_1}{k_7})^{\frac{1}{2}}(M)(CH_2O)$, $d(H_2)/dt$ may vary up to $\frac{1}{5}\, d(CH_3OH)/dt$, in fact as observed.

However, Klein's experiments in the baked and unbaked vessels showed that the change in $d(H_2)/dt$ could be as high as 100% of $d(CH_3OH)/dt$, much higher than the 20% allowed by this mechanism. Ke also observed a very large change in $d(H_2)/dt$, apparently related to vessel evacuation; prolonged evacuation resulted in suppression of hydrogen formation.

If the above mechanism is valid this would be due to other heterogeneous reactions occurring in the unconditioned vessel, such as reaction (3')

$$(3') \quad HCO + M \xrightarrow{wall} H + CO + M$$

From the stationary state expressions for the radical concentrations, an increase in k_3 will increase the concentration of hydrogen atoms; whereas there would be no effect upon the concentrations of HCO and CH_2OH, and no effect upon the initial rate of methanol formation. However, if a large fraction of the CH_2O is allowed to react the proportion of CH_3OH will be decreased. This interpretation appears to be consistent with the results of Klein's experiments 4 and 4a, and 1 and 1a (6). These results were interpreted by Klein as indirect evidence of methanol formation by a non-chain reaction.

Another proposal is that the rapid rate of hydrogen formation observed by Klein and by Ke is due to a molecular reaction on the surface of the unbaked or unconditioned reactor,

$$CH_2O \xrightarrow{wall} CO + H_2$$

The interpretations given above of course contradict the suggestion that initiation and termination are both at the surface in conditioned vessels. Although Klein did not mention whether or not his experiments using various S/V ratios and mixtures of CH_2O and CD_2O were done in baked vessels, reproducible results could be obtained in a baked vessel only. Therefore it is taken for granted that those experiments were done in the

conditioned (baked) vessel. Heterogeneous reactions, however, might have played an important role in the unbaked vessel but not in the baked vessel. Kallend and Purnell (24),in their work on the gas-phase thermal decomposition of dimethyl mercury, found that pre-treatment of the reaction vessels by washing with nitric acid, KCl-coating or carbon-coating could give homogeneous pyrolysis. If the vessel was washed with distilled water only the pyrolysis was heterogeneous. The active vessel can be inactivated by the above treatment, but only a certain number of runs can be carried out before the reactor becomes active again.

Since it seems that Klein's observations in the S/V ratio experiments are valid for the baked vessels only, it is doubtful that his proposal that both chain initiation and termination are wall effects is needed. The wall effects might actually result from a heterogeneous reaction in the unbaked reaction vessel only.

At low temperature $d(CH_3OH)/d(H_2)>1$ and at high temperature $d(H_2)/d(CH_3OH)>1$, requiring that for activation energies, $E_3>E_5$ and for frequency factors, $A_3>A_5$. A_3 is expected to be larger than A_5 because of the less complicated reacting species (see the discussion in section 2). Reaction (3) may have a higher activation energy than reaction (5), E_3 may be 26 kcal (9) and E_5 is expected to be around 6 kcal, as discussed before. In this mechanism, reactions (3) and (5)

compete with one another for the HCO radical, k_3 is greater than k_5 at high temperature and k_5 is greater than k_3 at low temperature. The limiting rate expressions at high temperature are

$$\frac{d(H_2)}{dt} = k_3\left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} (M)(CH_2O)$$

and $$\frac{d(CH_3OH)}{dt} \simeq 0$$

This is consistent with the results in shock waves (9), i.e. there is a homogeneous radical reaction at high temperature and H_2 and CO are the major products.

In the rate expressions, the rate of H_2 formation is pressure independent, fitting the observed inert gas effects.

Rate expressions for both H_2 and CH_3OH formation in the combined mechanism are almost the same as those obtained from their individual pyrolysis mechanism; and would be exactly the same when $k_3 >>> \frac{k_2k_5}{k_6}$. Therefore, the activation energies and frequency factors in combined mechanism would be the same as those estimated from the individual mechanisms.

PROPOSALS FOR FURTHER RESEARCH

Longfield reported the order for methanol formation with respect to formaldehyde to be 1.7 at 415° C. The orders obtained in the present work are 1.82 ± 0.05 and 2.09 ± 0.06 at 420° and 452° C respectively. From these data it seems that there is a temperature dependence of reaction order caused by some undetermined reaction. Further careful study might prove interesting.

Radical reactions of methanol may be detectable by pyrolyzing a mixture of CH_2O and CD_2O at low temperature (preferably 300~400°C). If radical reaction does not occur, i.e. the reaction is the elementary reaction

$$2\ CH_2O \rightarrow CH_3OH + CO,$$

four species of methanol, i.e. CH_3OH, CHD_2OH, CH_2DOD and CD_3OD which will yield m/e of 32, 34, 36 only can be expected. If the reaction follows a radical path, however the additional species, CD_3OH, CH_2DOH, CHD_2OD and CH_3OD would be produced, yielding mass number of 33 and 35. Since m/e 35 will not appear in the mass spectrometric pattern of the non-radical reaction, the radical reaction might be easily detected by this method.

The possible molecular reaction proposed above for formation of H_2 and CO could also be detected by pyrolyzing mixtures of CH_2O and CD_2O at higher temperature (500~600° C) in unbaked vessels. If the product contained no HD, or only a small amount of HD so that $(HD)^2/(H_2)(D_2)$ is smaller than the value obtained in the baked vessel, this probably would be an indication of a

molecular reaction occurring in the unbaked reactor.

An initial rate (less than 5% reaction) study of the pyrolysis of formaldehyde should be done in the baked and unbaked vessel at 500^{o} C. If there is no significant change in the rate of methanol formation one could conclude that the smaller amount of methanol formed in Klein's unbaked vessel is due to the rapid decrease in the concentration of CH_2O, due to faster hydrogen formation, and not due to inhibition of methanol formation.

BIBLIOGRAPHY

1. C.J.M. Fletcher, Proc. Roy. Soc. (London) A146, 357 (1934)

2. F. Patat, and H. Sachsse, Nachr. Ges Wis., Gottinger., Math-Physik Klasse (Fachgruppen III). 1, 41 (1935), as reported in reference (6).

3. E.W.R. Steacie and W.A. Alexander, J. Chem. Phys. 5, 372 (1937)

4. S. Kadama and Y. Takezaki, J. Chem. Soc. Japan, Pure Chem. Soc. 73, 13 (1952) as reported in reference (9).

5. J.E. Longfield and W.D. Walters, J. Am. Chem. Soc. 77, 6098 (1955). See also J.E. Longfield and W.D. Walters, J. Am. Chem. Soc. 77, 810 (1955)

6. R. Klein, M.D. Scheer, and L.J. Schoen. J. Am. Chem. Soc. 78, 50 (1956)

7. J.G. Calvert and E.W.R. Steacie., J. Chem. Phys., 19 176 (1951)

8. S.W. Benson and D.V.S. Jain, J. Chem. Phys. 31, 1008 (1959)

9. I.D. Gay, G.P. Glass, G.B. Kistiakowsky and H. Niki, J. Chem. Phys. 43 (11), 4017 (1965)

10. M. Eusuf and K.J. Laidler, Can. J. Chem. 42, 1851 (1964)

11. S.W. Benson, The Foundations of Chemical Kinetics, McGraw-Hill Book Co., Inc., New York. p. 380. 1960

12. R. Spence and W. Wild, J. Chem. Soc., 338 (1935)

13. R. Spence, J. Chem. Soc. 649,(1936)

14. P. Ke, The Thermal Decomposition of Glyoxal, Thesis, Memorial University of Newfoundland, 1968

15. K.J. Bombaugh and W.C. Bull, Analytical Chemistry, 34 (10), 1237 (1962)

BIBLIOGRAPHY (Continued)

16. J.E. Carruthers and R.G.W. Norrish, Trans. Faraday Soc. 32, 195 (1936)

17. K.J. Laidler, Chemical Kinetics, 2nd ed. McGraw-Hill Book Co.,Inc., New York, p. 391. 1965

18. P. Goldfinger, M. Letort and M. Niclause, "Contribution a l'etude de la structure moléculaire". Victor Henri Commemorative Volume, p. 283, Desoer, Liege, 1948

19. K.J. Laidler, Chemical Kinetics, 2nd ed. McGraw-Hill Book Co., Inc., New York, p. 390. 1965

20. K.J. Laidler, Chemical Kinetics, 2nd ed. McGraw-Hill Book Co., Inc., New York, p. 393, 1965

21. S.W. Benson, The Foundations of Chemical Kinetics. McGraw-Hill Book Co., Inc., New York, p. 281, 1960

22. K.H. Geib, Ergeb, Exakt, Naturwiss., 15, 44 (1936).

23. Data from JANAF Thermodynamics Tables (Dow Chemical Co., Midland, Michigan, 1960) and V.N. Kondratiev et al, Dissociation Energy of Chemical Bond, Ionization Potentials and Electron Affinities (Academy of Science, Moscow, 1962)

24. A.S. Kallend and J.H. Purnell, Trans. Faraday Soc., 93, 601, 1964

TABLE I

PRODUCTS AT LONG REACTION TIMES

Run #	Temp. ^{o}C	P_o^F mm	$(CH_2O)_o$ mmole	t sec	CO mmole	H_2 mmole	CH_3OH^a mmole	CH_3OH^b mmole	$\frac{a-b}{b}$ %
38	420	128	3.44	38700	1.264	0.277	1.005	0.987	2
39	420	128	3.44	35640	1.248	0.263	0.977	0.985	-1
49	452	132	3.30	79800	2.17	1.04	1.12	1.13	1
50	452	132	3.30	107280	2.15	1.03	1.10	1.12	-2

P_o^F Initial pressure of formaldehyde

a Result from vapor phase chromatographic analysis

b Obtained by subtracting n_{H_2} from n_{CO}, i.e. $n_{CH_3OH}{}^b = n_{CO} - n_{H_2}$

TABLE II

INITIAL RATE OF PYROLYSIS OF FORMALDEHYDE AT 420° C

Run #	P_o^F mm	$(CH_2O)_o$ mmole	t sec	CO mmole	H_2 mmole	CH_3OH^a mmole	CH_3OH^b mmole	R.C.[f] hrs
9	130	3.47	1200	0.160	0.050	e	0.110	12
10	128	3.43	1200	0.152	0.048	e	0.104	15
11	130	3.49	1200	0.165	0.061	0.104	0.104	20
12	130	3.48	1200	0.156	0.046	e	0.110	3
13	127	3.40	1200	0.155	0.050	0.104	0.105	26
14	128	3.43	1200	0.146	0.040	e	0.016	20
15	128	3.44	1200	0.113	0.025	0.091	0.088	40
16	126	3.38	1200	0.144	0.025	0.107	0.119	40
17	128	3.44	1200	0.147	0.044	0.106	0.103	20
18	22	0.60	3600	0.019	0.003	0.010	0.015	40
19	23	0.62	3600	0.016	0.003	0.011	0.012	20
20	21	0.57	3600	0.016	0.002	0.010	0.014	60
21	21	0.56	3600	0.013	0.002	0.010	0.011	18
22	21	0.56	3600	0.013	0.003	0.011	0.009	30
24	53	1.42	3600	0.030	0.007	0.024	0.023	20
25	51	1.38	3600	0.025	0.003	0.022	0.021	20
26	53	1.43	1500	0.024	0.003	0.021	0.021	20
27	80	2.14	1200	0.052	0.014	0.029	0.038	60
28[d]	82	2.21	1200	0.044	0.010	0.038	0.034	4
29	79	2.13	1200	0.062	0.023	0.036	0.039	24

(Continued)

TABLE II (Continued)

INITIAL RATE OF PYROLYSIS OF FORMALDEHYDE AT 420° C

Run #	P_o^F mm	$(CH_2O)_o$ mmole	t sec	CO mmole	H_2 mmole	CH_3OH^a mmole	CH_3OH^b mmole	R.C.[f] hrs
30	126	3.38	1200	0.117	0.022	0.096	0.095	24
31	129	3.46	1200	0.117	0.024	0.087	0.093	24
32[c]	54	1.45	1500	0.034	0.010	e	0.023	24
33[c]	128	3.44	1200	0.172	0.065	e	0.107	20
34	128	3.44	1200	0.110	0.017	e	0.090	36
35[c]	128	3.44	1200	0.144	0.068	e	0.075	30
36	128	3.44	1200	0.114	0.016	0.098	0.098	6
37	128	3.44	1200	0.112	0.021	0.101	0.099	20
40[c]	129	3.45	1200	0.125	0.029	e	0.096	24
41[c]	128	3.45	1200	0.130	0.040	e	0.090	20

a Result from vapor phase chromatographic analysis

b Obtained by subtracting n_{H_2} from n_{CO}

c 10 cm Hg inert gas, CO_2, added

d New sample of CH_2O was prepared and used after this run

e No data available

f Reactor conditioned

TABLE III

INITIAL RATE OF PYROLYSIS OF FORMALDEHYDE AT 452° C

Run #	P_o^F mm	$(CH_2O)_o$ mmole	t sec	CO mmole	H_2 mmole	CH_3OH^a mmole	CH_3OH^b mmole	R.C.[f] hrs
42[d]	132	3.39	900	0.284	0.042	0.225	0.242	20
43[d]	131	3.39	900	0.229	0.053	0.142	0.176	3
45	132	3.31	120	0.050	0.018	0.029	0.032	3
46	133	3.32	240	0.077	0.023	0.056	0.053	16
47	132	3.31	240	0.077	0.024	0.051	0.053	4
51[g]	132	3.31	480	0.137	0.037	0.092	0.100	20
52[c]	133	3.32	480	0.179	0.077	e	0.102	8
53	85	2.13	900	0.091	0.020	0.070	0.071	20
54	85	2.13	900	0.093	0.019	0.081	0.074	20
55	52	1.31	1500	0.052	0.010	0.044	0.042	20
56	52	1.31	1500	0.053	0.010	0.047	0.043	2
57	22	0.55	3600	0.024	0.005	0.015	0.019	17
58	21	0.53	3600	0.024	0.005	0.023	0.019	3
59[c]	22	0.55	3600	0.028	0.011	e	0.018	12

a, b, c, e, f (Refer to Table II)

d not initial rate reaction

g After this experiment the chamber temperature of VPC was lowered to 100° C instead of 120° C for better separation of CH_2O and CH_3OH peaks.

P_o^F Initial pressure of formaldehyde

FIGURE I

Diagram of Apparatus

T	Stopcocks
A1	Main trap
A2	Trap for analysis
V1,V2	Calibrated storage
D	Diffusion pump
F	Calibrated measuring flask
G	Spoon pressure gauge
R	Reaction vessel
M1	External manometer
M2	Gas burette
TP	Toepler pump
S	VPC sampling system
Sg	Formaldehyde storage
AF	Air furnace
O	CuO oxidation chamber

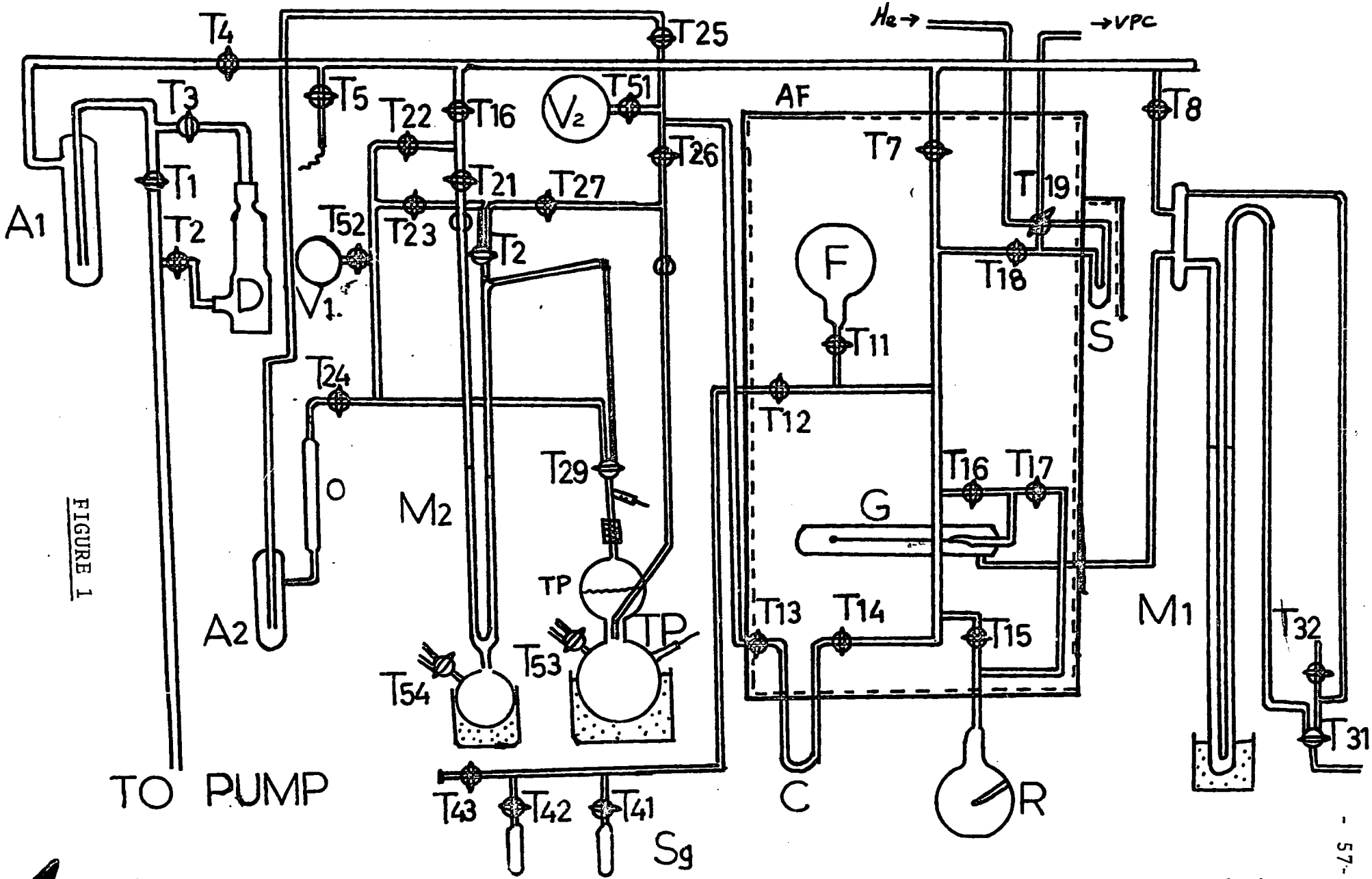
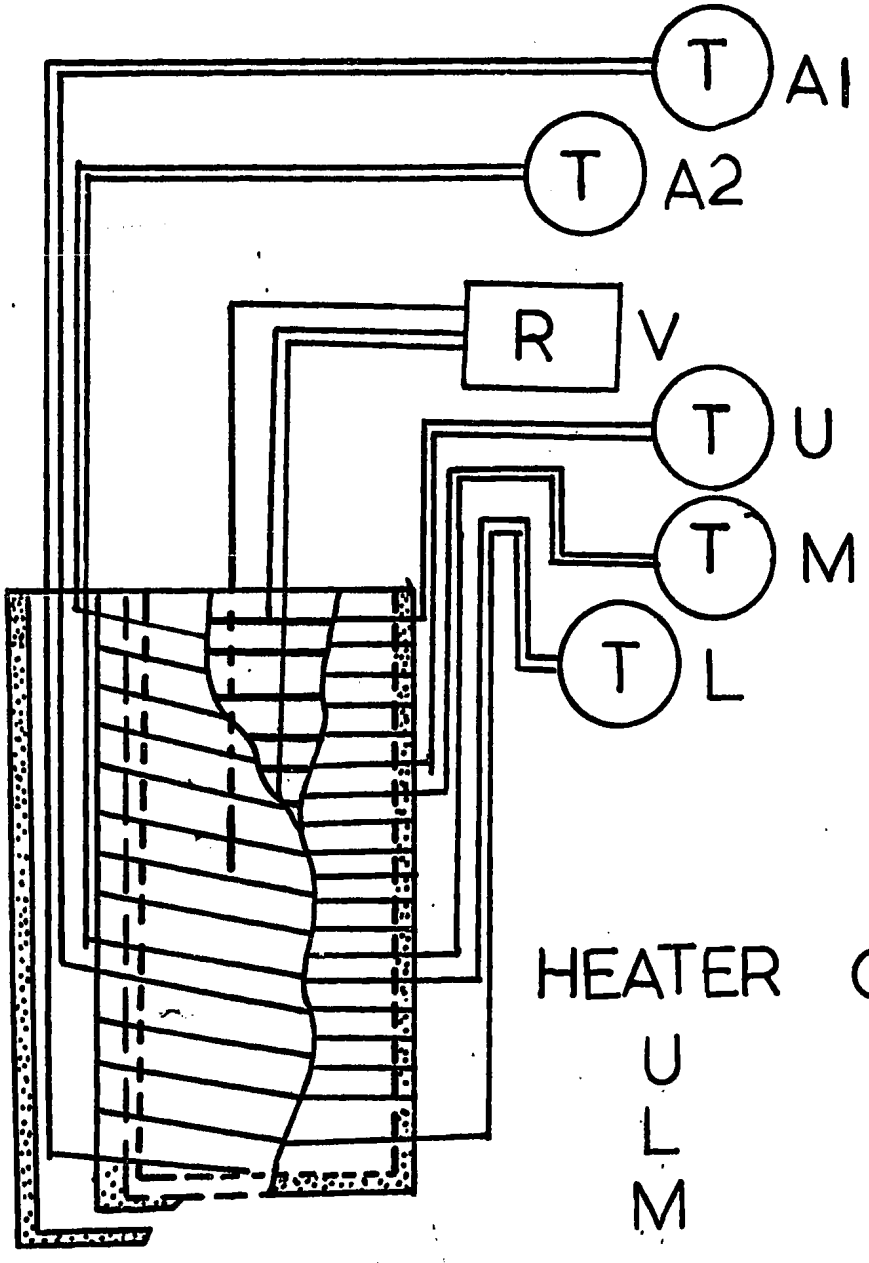

T4
T25
He→
→VPC
T3
T5
T22
T16
V2
T51
AF
T8
T1
T21
T27
T26
T7
T19
A1
T2
T52
T23
T2
F
T18
D
V1
T11
S
T24
T12
T29
T16
T17
O
M2
G
TP
A2
T13
T14
T15
M1
T32
TP
T53
T54
T31
TO PUMP
T43
T42
T41
C
R
Sg

FIGURE 1

FIGURE 2

Diagram of Furnace

FIGURE 2



HEATER	OHMS
U	16
L	16
M	15
V	32
A1	23
A2	21

T *Transformer*

R *Regulator*

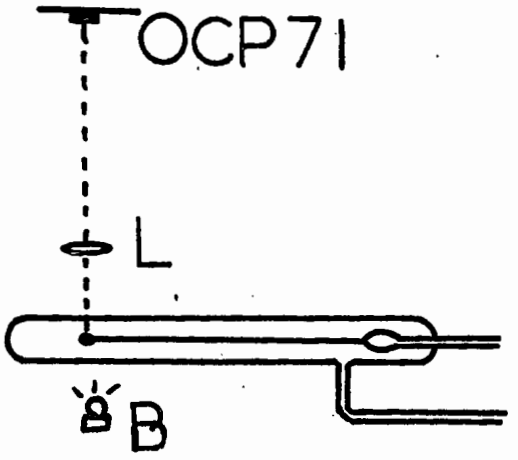
FIGURE 3

3A. Sketch of Spoon Pressure Gauge

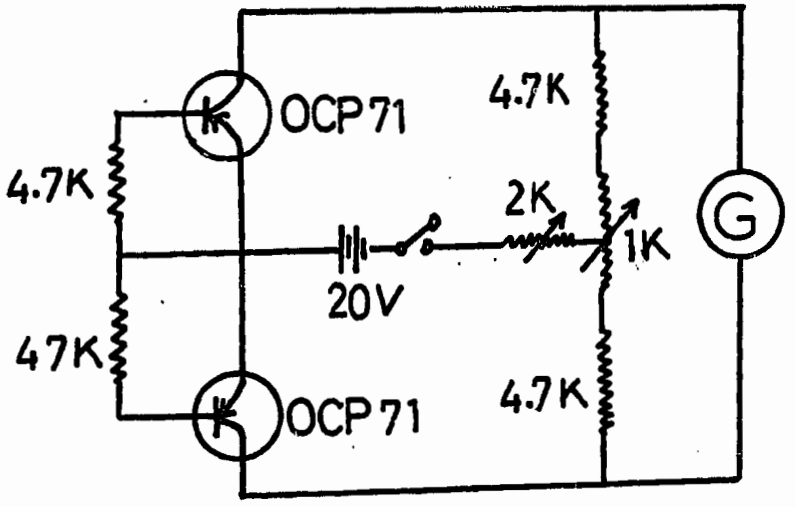
3B. Diagram of Detecting System

L	Concentrating Lens
B	Light Source
G	Galvanometer
OCP71	Phototransistor

FIGURE 3



3A



3B

FIGURE 4

Flow Sheet of Formaldehyde Preparation

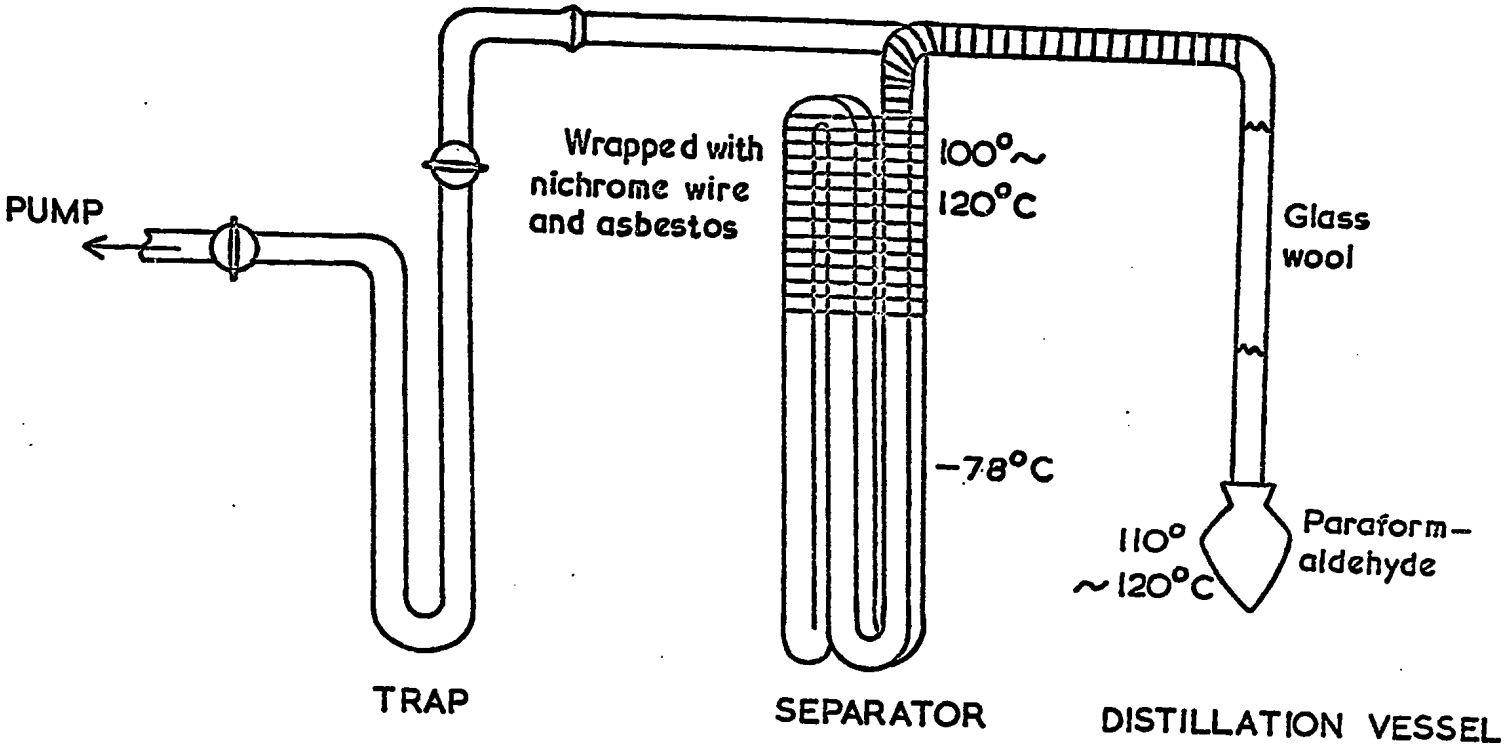

PUMP
Wrapped with nichrome wire and asbestos
100°~ 120°C
Glass wool
-78°C
110° ~120°C
Paraform-aldehyde
TRAP
SEPARATOR
DISTILLATION VESSEL

FIGURE 4

FIGURE 5

Reactor Thermocouples

FIGURE 5

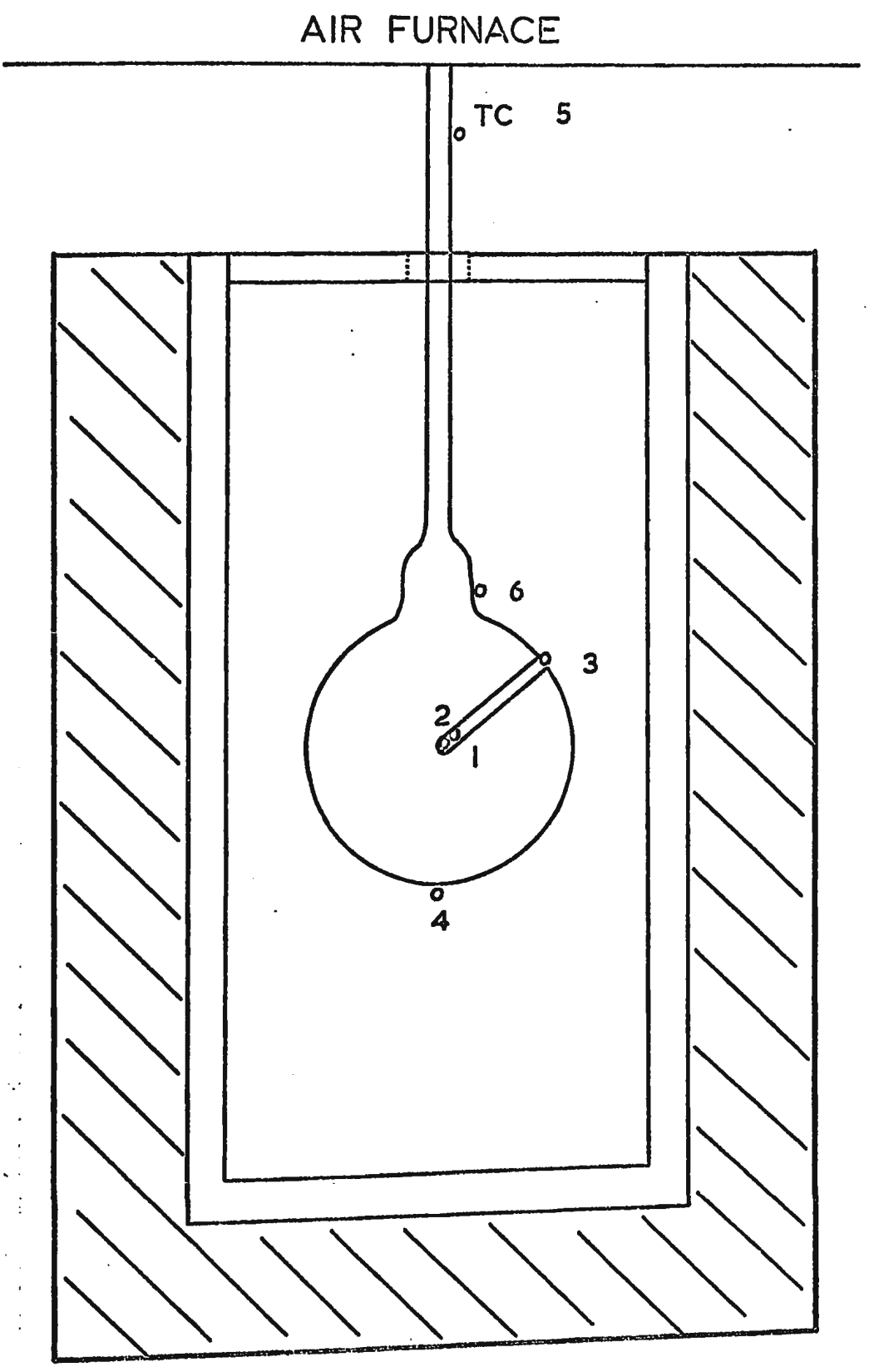


FIGURE 6

Plots of Log Initial Rate of CH_3OH (from $n_{MeOH} = n_{CO} - n_{H_2}$) Formation against Log Initial Concentration of HCHO and the Effect of 100 mm Added Foreign Gases at 420° C and 452° C.

○ Rate at 420° C

⊖ Rate showing the standard deviation of average of 13 experiments at 420° C

▽ Rate at 420° C with 100 mm inert gas CO_2 added

⊗ Rate at 452° C

△ Rate at 452° C with 100 mm inert gas CO_2 added

FIGURE 6

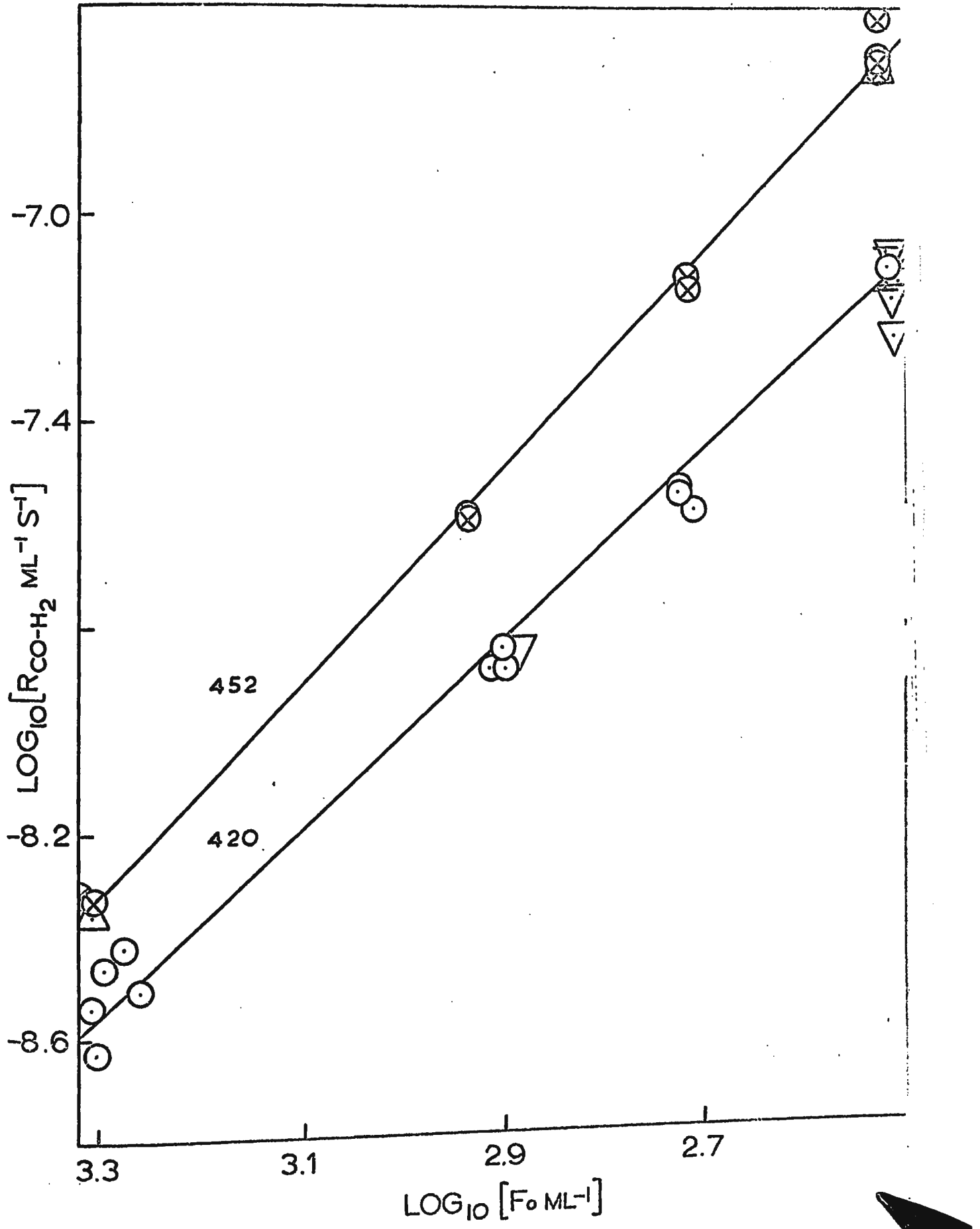


FIGURE 7

Plots of Log Initial Rate of Methanol

(from VPC analysis)

Formation at 420° and 452° C

○ Rate at 420° C

⊗ Rate at 452° C

FIGURE 7

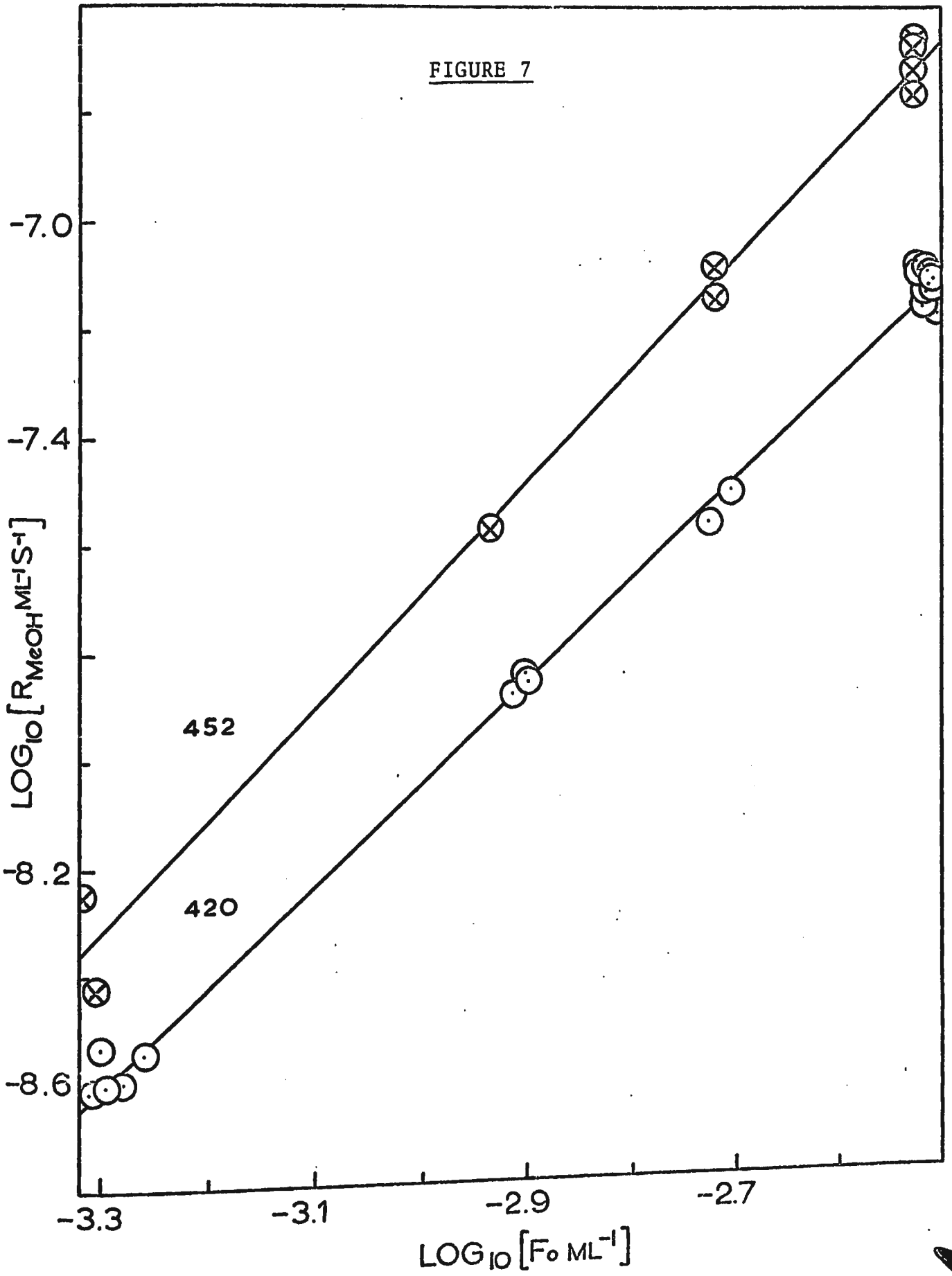


FIGURE 8

Plots of Log Initial Rate of Hydrogen Formation against Log Initial Concentration of Formaldehyde at 420° C and 452° C


Rate showing the standard deviation of average of 13 experiments at 420° C


Rate showing the standard deviation of average of 3 experiments at 420° C


Rate showing the standard deviation of average of 5 experiments at 420° C


Rate at 420° C with 100 mm inert gas CO_2 added


Rate showing the standard deviation of average of 4 experiments with 100 mm inert gas CO_2 added at 420° C


Rate showing the standard deviation of average of 4 experiments at 452° C


Rate at 452° C with inert gas CO_2 added

Rate at 452° C

FIGURE 8

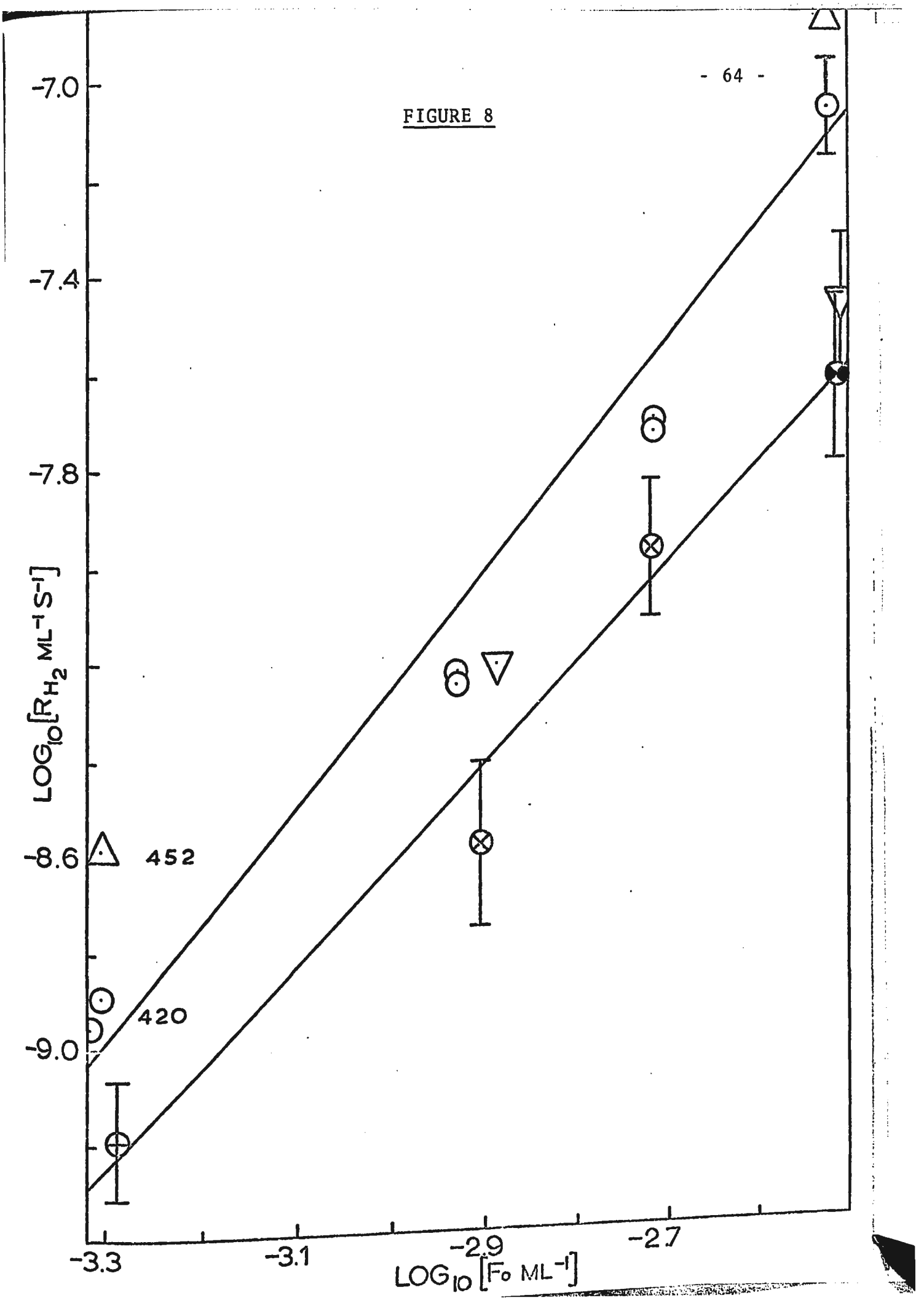


FIGURE 9

Plots of Induction Period of Hydrogen at 452° C

FIGURE 9

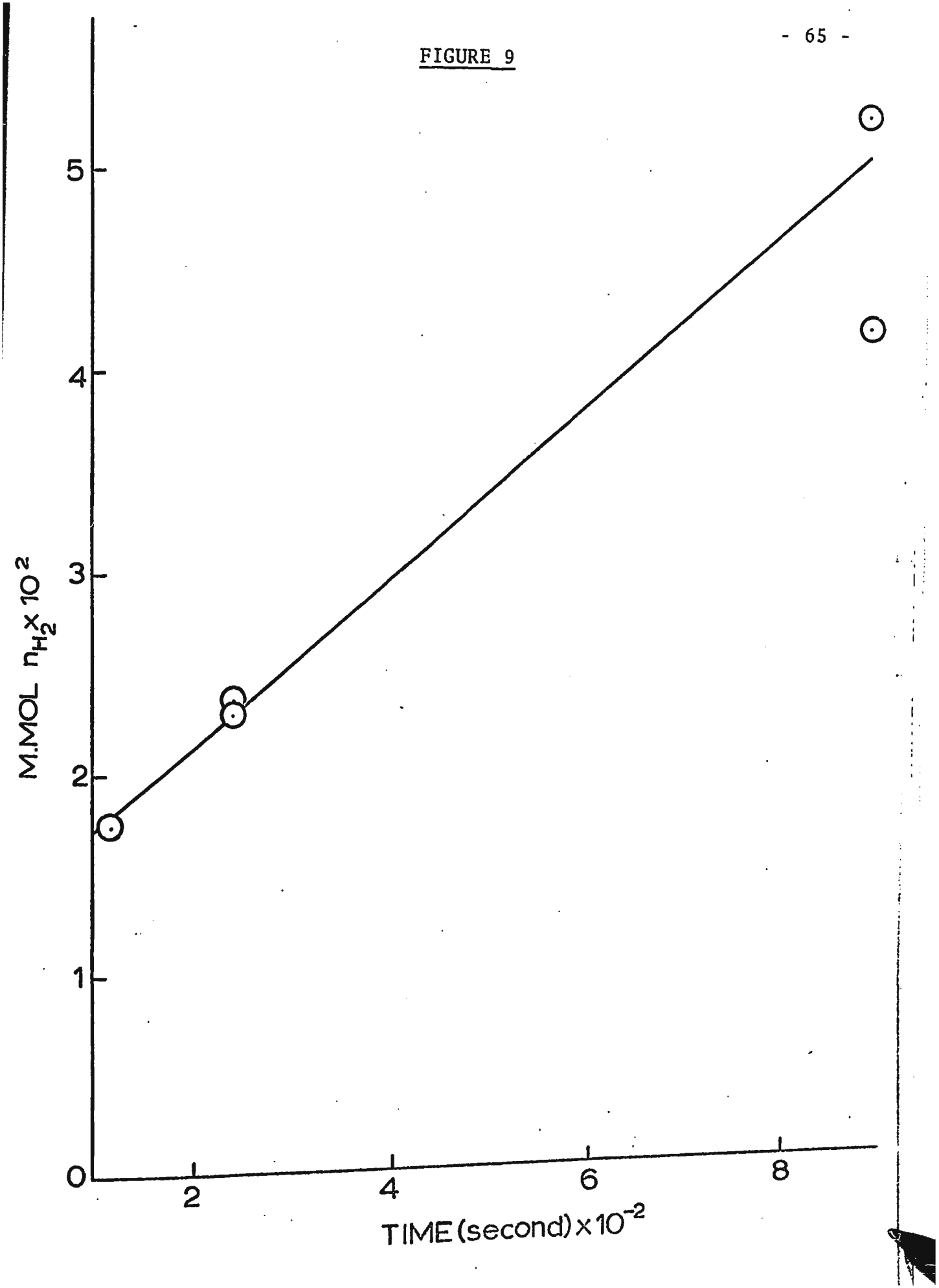


FIGURE 10

Calibration Chart of Formaldehyde

FIGURE 10

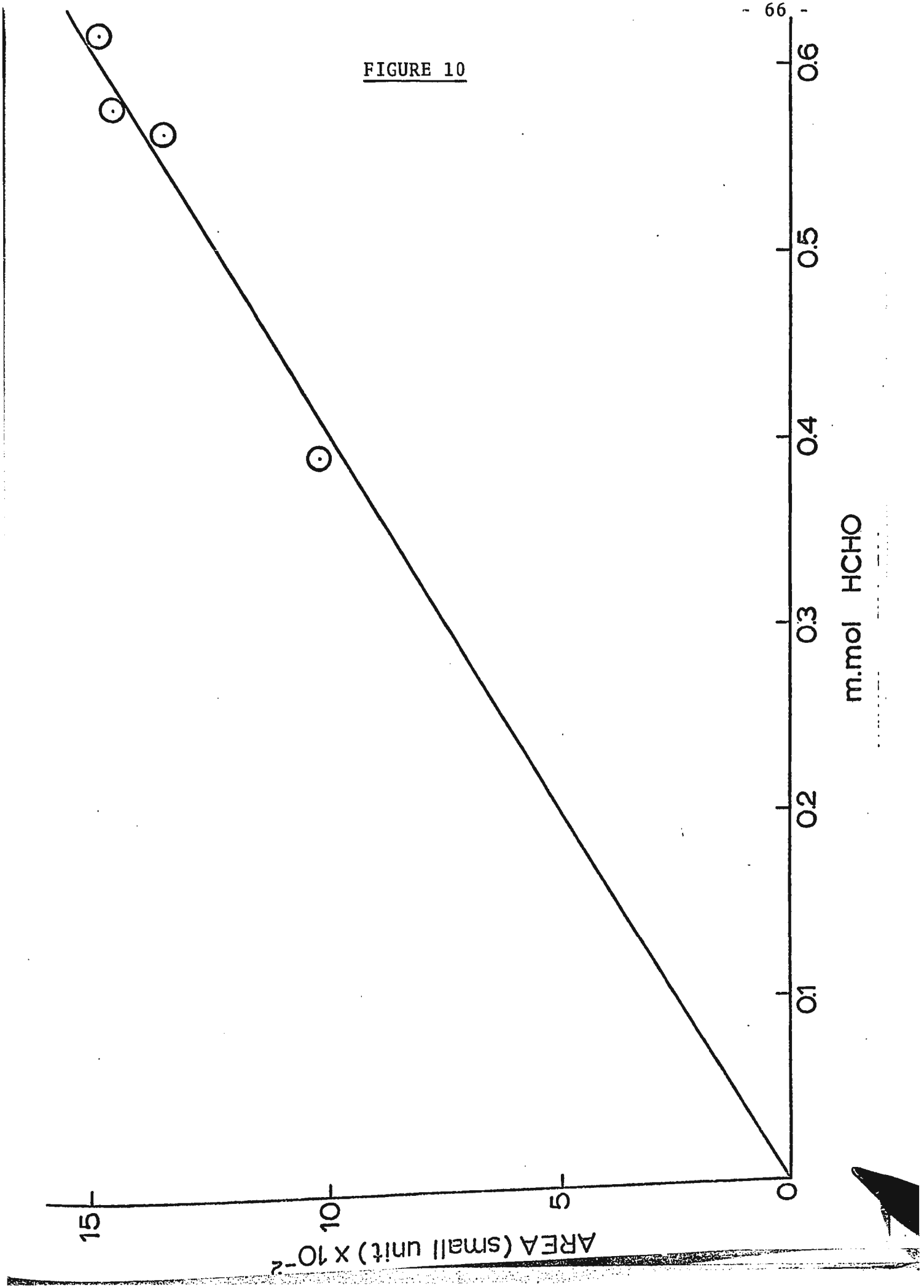
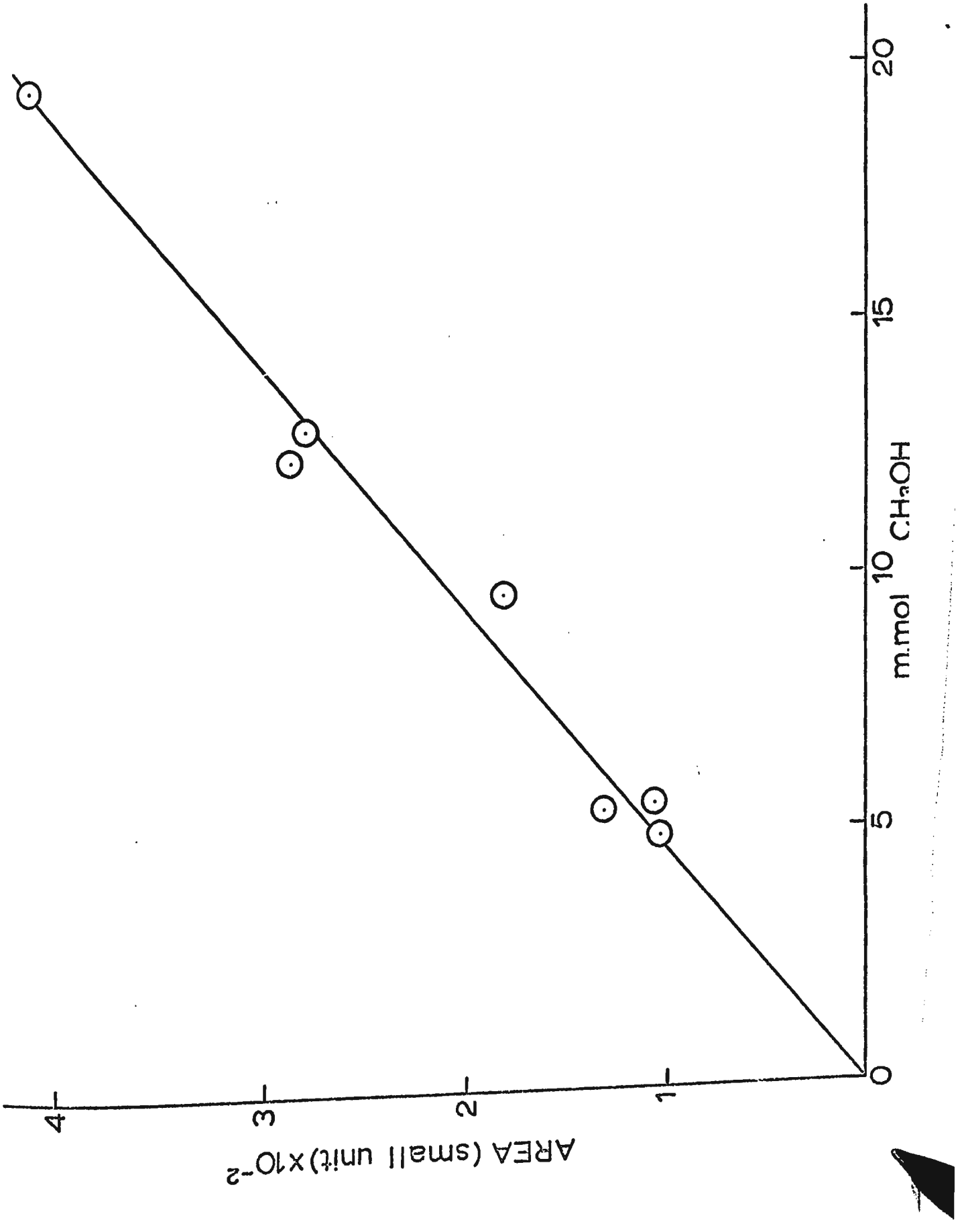


FIGURE 11

Calibration Chart of Methanol

FIGURE 11



APPENDIX

Referees' Comments and Reply

Comments (J.F. Ogilvie)

This dissertation incorporates the results and interpretation of repeated kinetic experiments at only two temperatures in an assembled apparatus previously constructed. The consistency of the results appears to make them reliable and the kinetic analysis which includes new modifications to previously published reaction schemes seems reasonably critical. The bibliography is rather limited, only twenty separate sources (including an unpublished one) being referred to. There is some confusion in terminology in that a particular radical species is apparently indiscriminately designated either H_2COH or H_3CO; although each of these is a characterised chemical species, and also each could plausibly occur in this chemical system, no discussion of this ambiguity appears in the text. Typographical and minor grammatical errors abound, and must be corrected; a list of those detected is appended. In summation, this dissertation is acceptable after the specified corrections have been effected.

Discussion of Dr. Ogilvie's Comments

The radical species H_2COH and H_3CO discussed in this thesis is designated as H_2COH. Benson et al, in their Further Studies of the Pyrolysis of Dimethyl Ether (8), show that the concentration of H_3CO is of the order of 0.05 CH_3. For the isomeric radical H_2COH, the estimated concentration is about the same as for CH_3. Therefore one might expect H_2COH to be a more important species in the system. Gay (9) detected the radical H_3CO but used H_2COH in discussing the reaction mechanism, perhaps implying that H_2COH is considered as a more probable species.

Questions (M.Z. Hoffmann)

1. The abstract states that the CH_3OH/H_2 ratio at 452^o is about 4 although the data of Table III do not show this ratio experimentally.

2. The slope of the log-log plots (Fig. 6 and 8) are used (P. 25-26) to determine the order of CH_3OH and H_2 production. How sensitive is the slope of such a plot to the experimental scatter? Taking the range of the data, the order for both may very well be 2 removing any question of a temperature dependence of the reaction order.

3. In the discussion section, no distinction is made in the numbering of the references and the equations which leads to some difficulty in reading and interpreting the material.

4. On P. 32, is there any reason for CH_3O to be written once as H_3CO?

5. At the bottom of P. 32 reference is made to radical chain mechanisms that lead to CH_3O. However, the equations that follow (steps 1, 3, 2, 4, 7) do not show production of CH_3O.

6. On the top of P. 33, has reaction 1 (P.32) been included in the rate law involving $-d[CH_2O]/dt$?

7. On P. 34-35, a statement is made: "All of these reactions are bimolecular hydrogen atom exchange reactions and have heats of formation of -49, -57, and -51 kcal, respectively". It is not clear what "heats of formation" of these reactions mean nor are there any references for the numbers quoted. Were these values measured by the candidate?

8. On P. 49 is the second place where the question of temperature dependence on reaction order is raised. It seems that a speculation on the "undetermined reaction" would be in order.

Discussion of Dr. Hoffman's Comments

1. According to the abstract, the CH_3OH/H_2 ratio at 452^o is about 1 (not 4). This is the result of the long reaction time experiment, as can be seen from Table I.

2. The sensitivity of the slope of the log-log plots (Figs. 6 and 8) to the experimental scatter calculated with an IBM 1620 computer, using the least squares treatment, are as shown on the first 5 lines of page 26. These results show that even if the high range of the data at 420^o and low range at 452^o are taken, the orders at both temperatures will still be 1.91 and 2.00 for CH_3OH, suggesting that there is a possible temperature dependence of reaction orders in methanol formation.

3. In the discussion section some numbering of references were left out to avoid repetition. For example, the references of Klein, Longfield, Gay and Ke were mentioned 8, 6, 5 and 3 times respectively. Since one reference number only was assigned to each of the above references in the bibliography

sheet, to avoid repetition, distinction was not made each time the reference appeared. As to equations, only those which need to be discussed further are numbered.

4. H_3CO refers to the same thing as CH_3O on P. 32.

5. The CH_3O Gay (9) mentioned in his paper is H_2COH radical which accounts for the step 1, i.e. initiation step.

6. With the long chain assumption, the rate of reaction 1 is considered as much slower than the chain propogating steps. Therefore, is is neglected in the rate law involving $-d[CH_2O]/dt$ on the top of P. 32.

7. The statements: "heats of formation" of -49, -57 and -51 on P.34-35 should read of "heats of reaction". These values of heats of reaction are quoted from reference 23.

8. Although a temperature dependence of reaction order is suggested, as mentioned in page 26 this difference in reaction orders between two different temperatures might be caused by some systematic experimental error. Therefore no reaction mechanism involving the

temperature dependence was discussed, in the absence of a more accurate method for methanol analysis.

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